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Exceptional activity of gallium(III) chloride and chlorogallate(III) ionic liquids for Baeyer–Villiger oxidation†

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Baeyer–Villiger oxidation of cyclic ketones, using H_2O_2 as the oxidising agent, was systematically studied using a range of metal chlorides in different solvents, and in neat chlorogallate(III) ionic liquids. The extremely high activity of $GaCl_3$ in promoting oxidation with H_2O_2, irrespective of solvent, was reported for the first time. The activity of all other metal chlorides was strongly solvent-dependent. In particular, $AlCl_3$ was very active in a protic solvent (ethanol), and tin chlorides, $SnCl_4$ and $SnCl_2$, were active in aprotic solvents (toluene and dioxane). In order to eliminate the need for volatile organic solvent, a Lewis acidic chlorogallate(III) ionic liquid was used in the place of $GaCl_3$, which afforded typically 89–94% yields of lactones in 1–120 min, at ambient conditions. Raman and ^{71}Ga NMR spectroscopic studies suggest that the active species, in both $GaCl_3$ and chlorogallate(III) ionic liquid systems, are chlorohydroxygallate(III) anions, $[GaCl_3OH]^-$, which are the products of partial hydrolysis of $GaCl_3$ and chlorogallate(III) anions; therefore, the presence of water is crucial.

Introduction

Baeyer–Villiger (BV) oxidation, in which linear or cyclic ketones are oxidised to esters or lactones, has been known for over 110 years.[1] It is particularly useful to generate lactones, used as intermediates for pharmaceuticals, herbicides and polymers, as well as solvents, flavours and fragrance additives.[1,2] Common oxidants in BV oxidation are peroxyacids, such as peroxyacetic or *m*-chloroperoxybenzoic. They are very active oxidants, but also intrinsically unstable and shock-sensitive, and thus expensive to store and transport, hazardous to use, and they produce acidic waste. All these factors drive the search for more sustainable oxidising agents.

Aqueous hydrogen peroxide, a much 'greener' alternative: it is more stable, therefore safer to use, and generates water as the oxidation by-product. Although H_2O_2 is characterised by a high content of active oxygen, it is kinetically inert, and requires an acidic catalyst to oxidise ketones.[2,3]

Lewis acids catalyse BV oxidation by coordinating to the carbonyl group of a ketone, thereby activating it towards the nucleophilic attack of hydrogen peroxide by increasing the polarisation of the C=O double bond.[2,4] A number of Lewis acidic metal chlorides ($AlCl_3$, $SnCl_4$, $FeCl_3$, $ZrCl_4$, $TiCl_4$ and $ZnCl_2$) have been used as catalysts in Baeyer–Villiger oxidation with H_2O_2 (as aqueous solution) or with silyl peroxides (which is a masked version of 100% H_2O_2).[3,5–10] However, the literature data are fragmentary, and it is not possible to directly compare the catalysts due to the use of different solvents, substrates and conditions. The most studied reaction is the oxidation of ketones with H_2O_2 catalysed by $AlCl_3$, both homogenously (in ethanol), and heterogeneously (on alumina or silica supports).[5–7] Less encouraging results were found using tin chlorides: $SnCl_4$ in methyl *t*-butyl ether was very weakly active in these oxidation of 2-adamantanone with H_2O_2, yielding only 3% conversion,[8] whereas $SnCl_2$ in butanol was found inactive in the oxidation with H_2O_2.[9] In contrast, $SnCl_4$, $AlCl_3$ and $FeCl_3$ were all active catalysts in BV oxidation with bistrimethylsilyl peroxide as an oxidising agent.[10]

Additionally, several organoselenium compounds, like bis[3,5-bis(trifluoromethyl)phenyl]diselenide,[11] 3,5-bis(perfluorooctyl)phenyl butylselenide,[12] diselenide bearing bistriflate[13] and dibenzyl diselenide[14] were used as catalysts for the Baeyer–Villiger oxidation with H_2O_2 (30 or 60% aq.). The oxidation of ketones were carried out generally at room temperature from 2 (for cyclobutanone) to 24 h (for larger cyclic ketones) giving high yields of lactones.

The very promising results with H_2O_2 as an oxidant were also achieved using molecular sieves modified with tin (Sn-Beta) or Sn(IV) centres incorporated into mesoporous MCM-41 (Sn–MCM-41) as catalysts, in dioxane at 90 °C.[8,15] Surprisingly,

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homogenous BV oxidation in dioxane with Lewis acidic chlorides has not been reported.

In the search for a sustainable BV oxidation, we have studied the use of ionic liquids, both as solvents and, more recently, as catalysts. In studying the solvent effect, it has been demonstrated that both conversion and reaction kinetics depended on the structure of ionic liquid or molecular solvent used.[16,17] Mildly Brønsted acidic, supported ionic liquids based on $[HSO_4]^-$, were active and recyclable catalysts for BV oxidation with H_2O_2 in dichloromethane.[16] Strongly Lewis acidic ionic liquids with chloroaluminate(III) anions were very potent catalysts for cyclobutanone oxidations with silyl peroxides.[17] Despite promising results, this work remains the only example of BV oxidation catalysed with Lewis acidic ionic liquids reported to-date.

Here, we aim to directly compare the catalytic performance of various metal chlorides in BV oxidation of model cyclic ketones with H_2O_2, and to investigate whether the performance of the most active metal chlorides could be further enhanced by using them in the form of chlorometallate ionic liquids, rather than as a solution in a molecular solvent.

Experimental

Materials and methods

All materials (metal chlorides, 1-butyl-3-methylimidazolium chloride, ketones) were purchased from Sigma-Aldrich. Metal chlorides were anhydrous (purity 99.99%, sealed under argon in glass ampoules).

Substituted cyclobutanones (3-phenylcyclobutanone and 3-butylcyclobutanone) were synthesised following a standard two-step procedure: a [2 + 2] cycloaddition of dichloroketene to the vinyl derivative, followed by the reduction of the resulting dichloroketones with zinc in acetic acid (see ESI† for the NMR spectra).[18]

GC analyses were performed using a PerkinElmer Clarus 500 gas chromatograph equipped with an SPB™-5 column (30 m × 0.2 mm × 0.2 μm).

^1H NMR spectra were recorded at 300 MHz or 600 MHz and ^{13}C NMR at 75 or 150 MHz (Varian system), respectively.

^{71}Ga NMR spectra were recorded at 300 K using a Bruker AvanceIII 400 MHz spectrometer. Samples were analysed neat, using d_6-dimethylsulfoxide capillaries as an external lock. A solution of $Ga(NO_3)_3$ hydrate in D_2O was used as an external reference ($\delta = 0$ ppm).

Table 1 Compositions of chlorometallate ionic liquids

		$[C_4mim]Cl$		MCl_x	
Ionic liquid	χ_{MCl_x}[a]	mmol	g	mmol	g
$[C_4mim]Cl–GaCl_3$	0.50	5.70	0.9956	5.70	1.0037
$[C_4mim]Cl–GaCl_3$	0.67	3.80	0.6637	7.59	1.3364
$[C_4mim]Cl–GaCl_3$	0.75	2.85	0.4978	8.54	1.5037
$[C_4mim]Cl–AlCl_3$	0.67	4.53	0.7913	9.06	1.2081

[a] χ_{MCl_x} – molar fraction of metal chlorides in ionic liquids.

Raman analyses were performed using a Perkin-Elmer Raman Station 400F, with a 785 nm focussed laser beam. All samples were studied in quartz cuvettes, with forty 2 second scans recorded for each sample.

Synthetic procedures

Chlorometallate(III) ionic liquids. Chlorometallate(III) ionic liquids were synthesised in a nitrogen-filled glovebox (MBraun labmaster dp, <0.3 ppm of H_2O and O_2). In a typical procedure,[19] 1-butyl-3-methylimidazolium chloride, $[C_4mim]Cl$, was placed in a vial (10 cm^3) equipped with a stirring bar. Then, metal(III) chloride (M = Al or Ga) was added slowly, in portions, to achieve the desired composition, and allowed to react until a homogenous liquid was formed (3 h, 60 °C, 1000 rpm). Exact amounts of reactants are shown in Table 1.

Oxidation of ketones in the presence of metal chlorides. Into a two-necked round-bottomed flask equipped with a septum, a condenser with a balloon filled with nitrogen, and a magnetic stirring bar, 2-adamantanone (0.1 g, 0.67 mmol) and metal chloride (0.008–0.017 g, 0.067 mmol) were placed. Then, a molecular solvent (5 cm^3, see Table 2) was added, followed by the slow addition of 30% aq. H_2O_2 (0.152 g, 1.34 mmol). The reactions were carried out at 40–90 °C, and monitored by GC.

Table 2 The influence of the metal chloride MCl_x structure on the oxidation of 2-adamantanone[a]

Solvent	MCl_x	Yield of lactone[b]/%
Dichloromethane 40 °C	$GaCl_3$	96
	$AlCl_3$	32
	$SnCl_2$	57
	$SnCl_4$	65
	$InCl_3$	43
	$TiCl_3$	25
	$TiCl_4$	12
	$ZnCl_2$	1
	$FeCl_3$	7
Toluene 90 °C	$GaCl_3$	99
	$AlCl_3$	12
	$SnCl_2$	98
	$SnCl_4$	96
	$InCl_3$	71
	$TiCl_3$	0
	$TiCl_4$	7
	$ZnCl_2$	66
	$FeCl_3$	1
Ethanol 70 °C	$GaCl_3$	75
	$AlCl_3$	94
	$SnCl_2$	57
	$SnCl_4$	78
	$InCl_3$	6
	$TiCl_3$	18
	$TiCl_4$	22
	$ZnCl_2$	23
	$FeCl_3$	4
1,4-Dioxane 90 °C	$SnCl_2$	83
	$SnCl_4$	83

[a] Reaction conditions: 2-adamantanone (0.67 mmol), H_2O_2 30% aq. (1.34 mmol), solvent 5 cm^3 catalyst 10 mol%, reaction time 6 h. [b] Yields determined by GC.

Oxidation of ketones in the presence of ionic liquids. Into a two-necked round-bottomed flask equipped with a septum, a condenser with a balloon filled with nitrogen, and a magnetic stirring bar, a ketone (0.094–0.234 g, 1.34 mmol) and ionic liquid (0.470–0.942 g, 1.34 mmol) were placed. Then, 30% aq. H_2O_2 (0.304 g, 2.68 mmol) was slowly added into the flask using a syringe. After the reaction completion (1–120 min), 2 cm^3 of water and 2 cm^3 of dichloromethane were added, and stirred vigorously (5 min). The organic phase was analysed by GC with decane as an internal standard. For the isolation of product, the reaction mixture was dissolved in water (2 cm^3), extracted with dichloromethane (6 × 5 cm^3) and concentrated. The yields of lactones after the purification using column chromatography with a short bed of Al_2O_3 (the conversion of ketone was 100%, and only the isolation of traces of ionic liquid was necessary) and dichloromethane as the eluent were 89–93%. 4-Oxatricyclo[4.3.1.13.8]undecan-5-one was isolated by the extraction of the post reaction mixture with toluene (10 × 2 cm^3). After vacuum drying, the lactone was purified by crystallisation from hexane–ethyl acetate. The structure and purity of all synthesised ketones and lactones were confirmed by ^{1}H and ^{13}C NMR analysis (ESI) and were essentially identical with published spectral data for authentic samples:

3-Phenylcyclobutanone.[18] (^{1}H-NMR, 300 MHz, $CDCl_3$, TMS): δ/ppm 3.22–3.27 (m, 2H), 3.44–3.50 (m, 2H), 3.66 (quint., J = 8.2 Hz, 1H), 7.20–7.38 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm 31.1, 57.4, 129.2, 129.3, 131.4, 146.3, 209.2.

3-Butylcyclobutanone.[18] (^{1}H-NMR, 300 MHz, $CDCl_3$, TMS): δ/ppm 0.92 (t, J = 6.8 Hz, 3H), 1.20–1.40 (m, 4H), 1.55–1.62 (m, 1H), 2.28–2.43 (m, 1H), 2.50–2.70 (m, 2H), 3.10–3.19 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm 13.9, 22.4, 23.8, 30.4, 35.9, 52.4, 208.6.

3-Phenyl-γ-butyrolactone.[18] (^{1}H NMR, 300 MHz, $CDCl_3$, TMS): δ/ppm 2.66 (dd, J = 17.5 Hz, 9.1 Hz, 1H), 2.92 (dd, J = 17.5 Hz, 8.1 Hz, 1H), 3.77 (quint., J = 8.4 Hz, 1H), 4.26 (dd, J = 8.9 Hz, 8.0 Hz, 1H), 4.67 (dd, J = 9.0 Hz, 7.9 Hz, 1H), 7.16–7.27 (m, 2H), 7.27–7.33 (m, 1H), 7.33–7.34 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 35.7, 41.1, 74.0, 126.7, 127.7, 129.1, 139.4, 176.3.

3-Butyl-γ-butyrolactone.[18] (^{1}H NMR, 300 MHz, $CDCl_3$, TMS): δ/ppm 0.92 (t, J = 6.9 Hz, 3H), 1.15–1.30 (m, 4H), 1.43–1.52 (m, 2H), 2.14–2.33 (m, 2H), 2.49–2.66 (m, 2H), 3.89–3.95 (m, 1H), 4.39–4.44 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm 13.8, 22.4, 29.4, 32.7, 34.4, 35.6, 73.3, 177.2.

γ-Butyrolactone.[20] (^{1}H-NMR, 300 MHz, $CDCl_3$, TMS): δ/ppm 2.13–2.24 (m, 2H), 2.38–2.44 (m, 2H), 4.27 (t, J = 7.4 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm 22.3, 28.0, 68.8, 178.1.

4-Oxatricyclo[4.3.1.13.8]undecan-5-one.[20] (^{1}H-NMR, 300 MHz, $CDCl_3$, TMS): δ/ppm 1.70–2.15 (m, 12H), 3.01–3.12 (m, 1H), 4.39–4.52 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 25.8, 30.9, 33.7, 35.7, 41.2, 73.1, 178.2.

2-Oxabicyclo[3.2.1]octan-3-one.[20] (^{1}H-NMR, 300 MHz, $CDCl_3$, TMS): δ/ppm 1.65–2.25 (m, 7H), 2.40–2.80 (m, 2H), 4.82–4.89 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 29.1, 31.7, 32.4, 35.7, 40.5, 80.9, 170.7.

ε-Caprolactone.[20] (^{1}H-NMR, 600 MHz, $CDCl_3$, TMS): δ/ppm 1.72–1.87 (m, 4H), 1.88 (dd, J = 5.3 Hz, 2.6 Hz, 2H), 2.62–2.67 (m, 2H), 4.21–4.26 (m, 2H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ/ppm 22.9, 28.9, 29.3, 34.5, 69.2, 176.4.

4-Methyl-ε-caprolactone.[21] (^{1}H-NMR, 300 MHz, $CDCl_3$, TMS): δ/ppm 0.94 (d, J = 6.6 Hz, 3H), 1.80–1.92 (m, 5H), 2.55–2.71 (m, 2H), 4.15–4.25 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ/ppm 18.8, 21.6, 34.2, 36.7, 40.2, 67.5, 175.5.

4-Ethyl-ε-caprolactone.[22] (^{1}H NMR, 600 MHz, $CDCl_3$, TMS): δ/ppm 0.92 (t, J = 7.5 Hz, 3H), 1.40–1.28 (m, 3H), 1.57–1.43 (m, 2H), 1.93 (dddt, J = 15.1, 7.5, 3.6, 2.0 Hz, 1H), 2.03–1.96 (m, 1H), 2.61 (ddd, J = 14.1, 12.4, 2.1 Hz, 1H), 2.69 (ddd, J = 14.1, 7.6, 1.7 Hz, 1H), 4.18 (dd, J = 12.8, 10.1 Hz, 1H), 4.31 (ddd, J = 12.7, 5.9, 1.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 11.14, 28.38, 28.98, 33.02, 34.83, 41.73, 68.05, 176.01.

4-Propyl-ε-caprolactone.[22] (^{1}H NMR, 600 MHz, $CDCl_3$, TMS): δ/ppm 0.90 (t, J = 7.2 Hz, 3H), 1.38–1.22 (m, 6H), 1.53–1.44 (m, 1H), 1.67–1.57 (m, 2H), 1.92 (dddd, J = 16.0, 7.6, 3.8, 1.9 Hz, 1H), 2.01–1.95 (m, 1H), 2.61 (ddd, J = 14.1, 12.3, 2.1 Hz, 1H), 2.68 (ddd, J = 14.0, 7.6, 1.7 Hz, 1H), 4.18 (dd, J = 12.9, 10.4 Hz, 1H), 4.30 (ddd, J = 12.9, 6.0, 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 13.97, 19.70, 28.74, 33.04, 35.20, 38.50, 39.75, 68.05, 176.08.

4-tert-Butyl-ε-caprolactone.[23] (^{1}H NMR, 600 MHz, $CDCl_3$, TMS) δ/ppm 0.90 (s, 9H), 1.41–1.30 (m, 2H), 1.57–1.47 (m, 1H), 2.11–1.99 (m, 2H), 2.62–2.53 (m, 1H), 2.71 (ddd, J = 14.2, 7.5, 1.2 Hz, 1H), 4.16 (dd, J = 12.9, 10.5 Hz, 1H), 4.34 (ddd, J = 12.9, 6.0, 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 23.76, 27.43, 30.33, 32.98, 33.45, 50.77, 68.62, 176.29.

4-Phenyl-ε-caprolactone.[24] (^{1}H NMR, 600 MHz, $CDCl_3$, TMS): δ/ppm 1.89–1.80 (m, 1H), 2.11–1.99 (m, 2H), 2.17–2.11 (m, 1H), 2.88–2.73 (m, 3H), 4.32 (dd, J = 12.8, 10.3 Hz, 1H), 4.39 (ddd, J = 13.0, 5.5, 2.0 Hz, 1H), 7.17–7.20 (m, 2H), 7.25–7.21 (m, 1H), 7.34–7.30 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 30.33, 33.69, 36.75, 47.25, 68.20, 126.57, 126.84, 128.75, 144.92, 175.58.

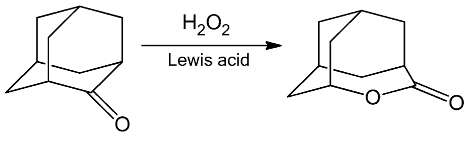
Isopropyl propanoate.[25] (^{1}H NMR, 600 MHz, $CDCl_3$, TMS): δ/ppm 1.11 (t, J = 7.6 Hz, 3H), 1.22 (d, J = 6.3 Hz, 6H), 2.28 (q, J = 7.6 Hz, 2H), 5.00 (dt, J = 12.5, 6.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 9.11, 21.78, 27.93, 67.45, 176.11–174.37.

p-Methoxyphenyl acetate.[26] (^{1}H NMR, 600 MHz, $CDCl_3$, TMS): δ/ppm 2.28 (s, 2H), 3.79 (s, 2H), 6.89 (d, J = 9.1 Hz, 1H), 7.00 (d, J = 9.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm 21.02, 55.55, 114.44, 122.28, 144.17, 157.23, 169.87.

Results and discussion

Screening of metal chlorides

Metal chlorides were used as Lewis acidic catalysts in a model oxidation of 2-adamantanone (Scheme 1) with a two-fold molar excess of H_2O_2 (30% aq.), at 10 mol% metal chloride loading.



Scheme 1 Model Baeyer–Villiger oxidation of 2-adamantanone.

Each metal chloride was tested in three solvents: dichloromethane, ethanol and toluene. Additionally, tin chlorides were tested in 1,4-dioxane.

The observed catalytic activity was strongly dependent the metal chloride, the solvent, and the reaction temperature (Table 2). In agreement with the literature, high yield of lactone was obtained using $AlCl_3$ in ethanol, but not with less polar and aprotic solvents.[5] In contrast, the previously unstudied $GaCl_3$ was the most active catalyst under all conditions. Moreover, $SnCl_2$ and $SnCl_4$ were very active in toluene and 1,4-dioxane, but not in ethanol and dichloromethane. These observations may explain the previously reported low activity of tin chlorides.[8,9] Other metal chlorides ($InCl_3$, $ZnCl_2$, $TiCl_3$, $TiCl_4$, $FeCl_3$) exhibited much lower activity, with an unpredictable dependence on the solvent.

The high catalytic activity of $GaCl_3$ was most likely related to its high solubility in the reaction mixtures, compared to other metal halides, which resulted in favourable reaction kinetics. Kinetic studies of selected catalytic systems (Fig. 1) revealed superior performance of $GaCl_3$, even at a lower temperature (40 °C).

Screening of chlorogallate(III) ionic liquids

Seeking to additionally improve the reaction sustainability by the removal of volatile organic solvents, and in the hope of further enhancement in the reaction rate, chlorogallate(III) ionic liquids were studied as Lewis acidic catalysts.

Chlorogallate(III) ionic liquids are synthesised by the reaction of anhydrous $GaCl_3$ with an organic chloride salt. Various molar fractions of $GaCl_3$, expressed as χ_{GaCl_3}, can be used to prepare homogenous ionic liquids.[19] For $\chi_{GaCl_3} < 0.50$, a neutral $[GaCl_4]^-$ anion coexists with Lewis basic chloride anion; for $\chi_{GaCl_3} > 0.50$, multinuclear chlorogallate(III) anions: $[Ga_2Cl_7]^-$ and $[Ga_3Cl_{10}]^-$ are formed, which impart strong Lewis acidity to these systems.[27] At the ideally neutral composition, $\chi_{GaCl_3} = 0.50$, only $[GaCl_4]^-$ is present. Compared to chloroaluminates(III), chlorogallates(III) offer equal or stronger Lewis acidity, as quantified by acceptor number (AN) approach,[27] and are more resistant to hydrolysis. Neutral chlorogallates(III) ($\chi_{GaCl_3} = 0.50$) have been used as solvents and co-catalysts in palladium-catalysed hydroethoxycarbonylation[28] and acetal formation,[29] whereas Lewis acidic systems ($\chi_{GaCl_3} = 0.67, 0.75$) catalysed arene carbonylation,[30] and oligomerisation of alkenes to lubricant base oils.[31] In general, however, applications of chlorogallate(III) systems are relatively poorly explored compared to their chloroaluminate(III) analogues.

Three compositions of chlorogallate(III) ionic liquids were used: $\chi_{GaCl_3} = 0.50$, 0.67 and 0.75, which corresponds to three different chlorogallate(III) anions, dominant in the respective compositions: $[GaCl_4]^-$ (neutral, as a benchmark), $[Ga_2Cl_7]^-$ (Lewis acidic), and $[Ga_3Cl_{10}]^-$ (Lewis acidic). All ionic liquids were based on 1-butyl-3-methylimidazolium cation, $[C_4mim]^+$. Results of a model oxidation of 2-adamantanone with a two-fold molar excess of H_2O_2 (30% aq.) are presented in Table 3. In order to form a homogenous reaction medium, equimolar amounts of ketone and ionic liquid (based on cation) were typically required. Depending on the anionic speciation, this resulted in molar excess of gallium metal to substrate between 1 and 3. Hence, the reactions in the ionic liquids contained at least ten times the concentration of metal than the equivalent reactions in molecular solvents. Nevertheless, this does not account for the significantly greater activity of the ionic liquid.

Using the ionic liquid with the highest $GaCl_3$ concentration ($\chi_{GaCl_3} = 0.75$) and the highest Lewis acidity (expressed as acceptor number, AN = 107.5), the oxidation was remarkably fast, reaching 99% yield of lactone and ketone conversion, in less than 1 min at ambient temperature. This contrasts with solutions of $GaCl_3$ in molecular solvents, which took more than two orders of magnitude longer, at elevated temperatures, to produce comparable yields.

The chlorogallate(III) ionic liquid with lower $GaCl_3$ concentration ($\chi_{GaCl_3} = 0.67$) and slightly lower Lewis acidity (AN = 99.5) was also slightly less active. Nevertheless, it still displayed extremely high catalytic activity, yielding 93% lactone yield after 1 min at ambient temperature. In contrast, no conversion was

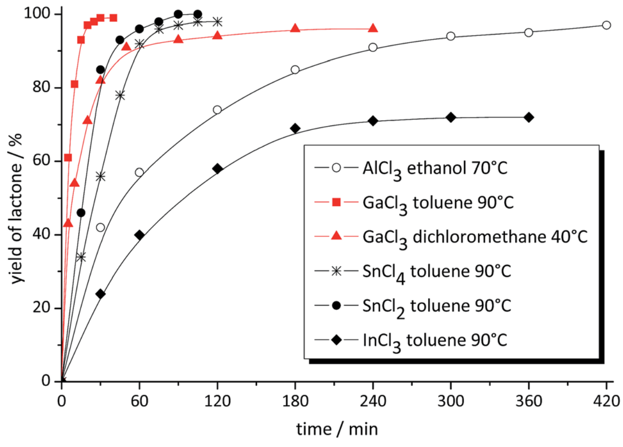


Fig. 1 Kinetics of the oxidation of 2-adamantanone (0.67 mmol), with H_2O_2 30% aq. (1.34 mmol) in solvent (5 cm^3), in the presence of MCl_x (10 mol%).

Table 3 The influence of chlorometallate(III) ionic liquids as catalysts for 2-adamantanone oxidation with H_2O_2 30% aq., at ambient temperature[a]

Ionic liquid	IL^b/mol%	Time/min	Yield of lactone^c/%
$[C_4mim]Cl–GaCl_3$, $\chi = 0.75$	25	1	99
	50	1	99
	100	1	99
$[C_4mim]Cl–GaCl_3$, $\chi = 0.67$	100	1	93
$[C_4mim]Cl–GaCl_3$, $\chi = 0.50$	100	1	0
		60	15
		300	43
$[C_4mim]Cl–AlCl_3$, $\chi = 0.67$	100	1	0
		60	11
		300	11

[a] Reaction conditions: 2-adamantanone (0.67 mmol), H_2O_2 30% aq. (1.34 mmol), RT. [b] Relative to ketone. [c] Yields determined by GC.

Table 4 The influence of oxidation agent on the oxidation of 2-adamantanone in the presence of the chlorogallate(III) ionic liquid[a]

Oxidant	Oxidant[b]/mol%	Time/min	Yield of lactone[c]/%
H_2O_2 30% aq.	200	1	99
	150	1	98
	110	1	87
H_2O_2 60% aq.	200	1	99
UHP	200	60	80
UHP 30% aq.[d]	200	1	92
$PhC(CH_3)_2OOH$	200	60	3
^{t}BuOOH in water	200	60	5
^{t}BuOOH in decane	200	60	0

[a] Reaction conditions: 2-adamantanone (0.67 mmol), $[C_4mim]Cl–GaCl_3$, $\chi_{GaCl_3} = 0.75$ (0.67 mmol), RT. [b] Relative to ketone. [c] Yields determined by GC. [d] 30% concentration of H_2O_2 in the solution.

detected under the same reaction conditions in the presence of the neutral chlorogallate(III) ionic liquid ($\chi_{GaCl_3} = 0.50$). Upon prolonged reaction time some reactivity occurred (43% lactone yield after 300 min), possibly due to hydrolysis of $[GaCl_4]^-$, resulting in catalysis by the evolved hydrogen chloride.

For comparison, strongly Lewis acidic chloroaluminate(III) ionic liquids were used as catalysts ($\chi_{AlCl_3} = 0.67$, AN = 95.6), at the same temperature. Very low yields of lactone (11%) were obtained, even after 300 min. This is in agreement with some of the results recorded for catalysis with metal chlorides (Table 2), where the performance of $AlCl_3$ was inferior to that of $GaCl_3$.

Screening of oxidising agents

The catalytic activity of $[C_4mim]Cl–GaCl_3$ ($\chi_{GaCl_3} = 0.75$) was tested in the presence of a range of oxidising agents. Results for two concentrations of H_2O_2 in water (30 and 60%) were compared to oxidations using the anhydrous urea·H_2O_2 complex (UHP), cumyl hydroperoxide (neat), and *tert*-butyl hydroperoxide, used as solutions in water and in decane (Table 4). Equimolar amounts of ionic liquid (based on the cation) and ketone were used in all cases.

Using decreasing amounts of H_2O_2 (30% aq.), it was demonstrated that the ratio of oxidising agent could be decreased from two-fold to nearly equimolar, without significant product loss. Decreasing water content (*i.e.* increasing H_2O_2 concentration to 60%) had no observable effect on conversion and yield, compared to using 30% aqueous solution of H_2O_2. However, replacing aqueous solution with anhydrous UHP complex (with formal H_2O_2 concentration of 36%), led to a dramatic decrease in the lactone yield (80% after 60 min). To confirm the beneficial role of water, the reaction with UHP was repeated in the presence of 0.1 g of water (giving formal H_2O_2 concentration of *ca.* 30%), with resulted in 92% lactone yield after 1 min. This confirmed that the presence of water is crucial for the observed high reaction rates in gallium(III)-promoted BV oxidation with H_2O_2. Interestingly, this is in direct opposition to earlier views, whereby water was detrimental for metal-catalysed BV oxidation, which was considered suitable only for anhydrous conditions.[2]

In BV oxidation, H_2O_2 is known to be a less active oxidant than peracids, but more active than hydroperoxides.[2,3] Considering the excellent performance of gallium(III) catalysts in H_2O_2 oxidation, it was anticipated that they may also catalyse oxidation by hydroperoxides. However, irrespective of the solvent (neat, water, aprotic solvent – see Table 4), hydroperoxides remained inactive in the model oxidation catalysed by the chlorogallate(III) ionic liquids.

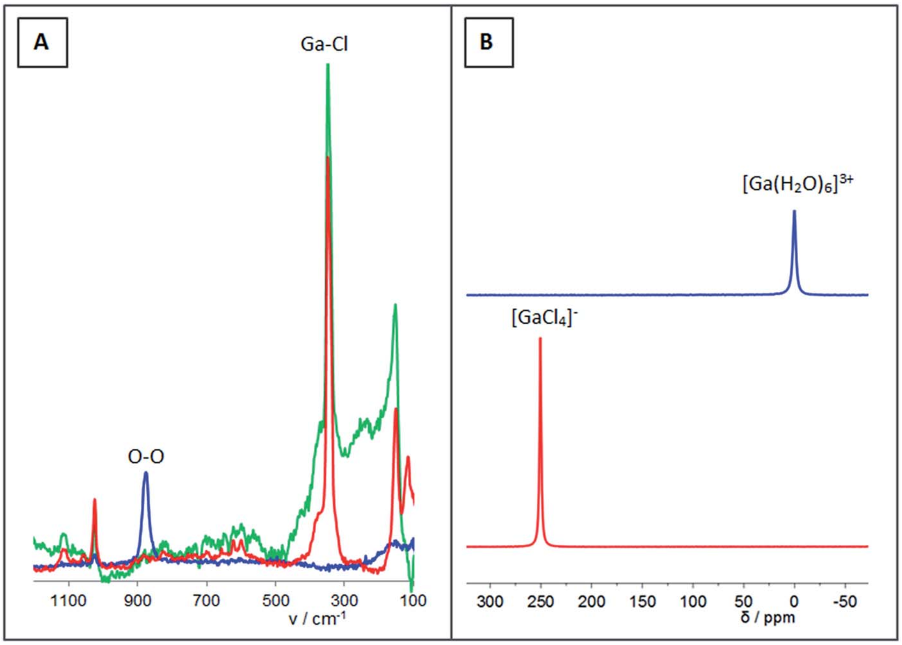


Fig. 2 (A) Raman spectra of $[C_4mim]Cl–GaCl_3$ $\chi_{GaCl_3} = 0.50$ (green), water phase (navy blue) and organic phase (red) after reaction with H_2O_2; (B) ^{71}Ga NMR spectra of water phase (navy blue) and organic phase (red) of $[C_4mim]Cl–GaCl_3$ $\chi_{GaCl_3} = 0.50$ after addition of H_2O_2.

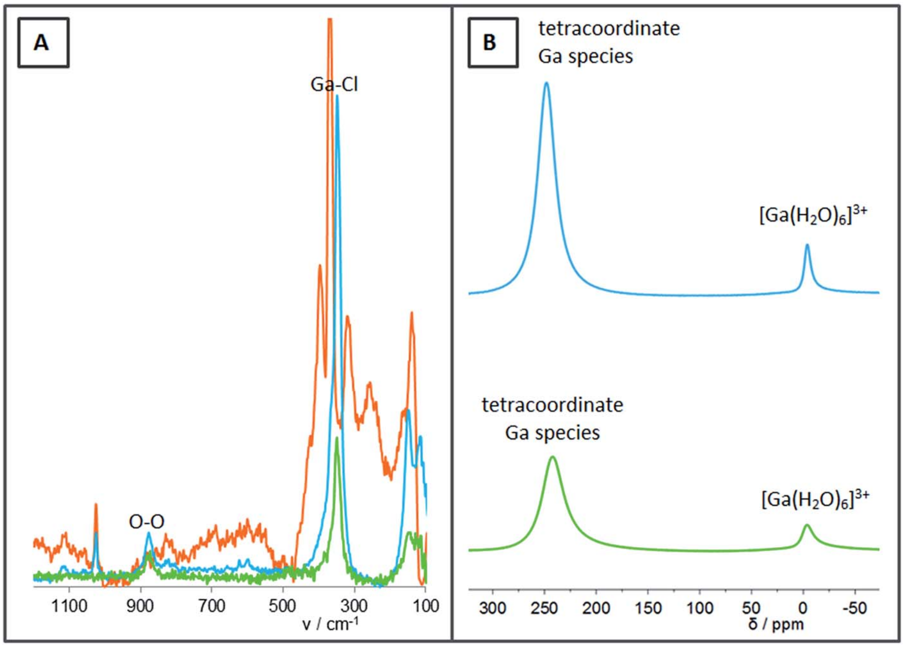


Fig. 3 (A) Raman spectra of [C_4mim]Cl–$GaCl_3$ $\chi_{\mathrm{GaCl_3}} = 0.75$ (orange), [C_4mim]Cl–$GaCl_3$ $\chi_{\mathrm{GaCl_3}} = 0.75$ after reaction with H_2O_2 (blue) and of the mixture $GaCl_3$–H_2O_2 (green); (B) ^{71}Ga NMR spectra of [C_4mim]Cl–$GaCl_3$ $\chi_{\mathrm{GaCl_3}} = 0.75$ after reaction with H_2O_2 (blue) and of the mixture $GaCl_3$–H_2O_2 (green).

Mechanistic considerations

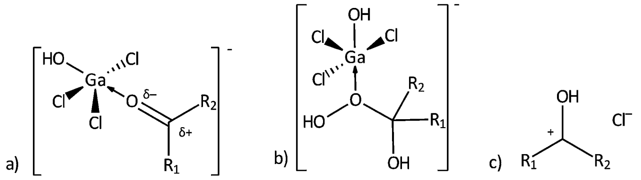
Screening studies revealed that gallium(III) chloride and chlorogallate(III) ionic liquids were much more active catalysts in BV oxidation with aqueous H_2O_2 than their aluminium(III) analogues. A combination of Raman and ^{71}Ga NMR spectroscopic studies was used to shed some light on the activation process. Two active systems were investigated: $GaCl_3$ and the chlorogallate(III) ionic liquid ($\chi_{\mathrm{GaCl_3}} = 0.75$), both as mixtures with aqueous H_2O_2 (molar ratio 1 : 1). As a comparison, aqueous H_2O_2 solutions of the inactive, neutral chlorogallate(III) ionic liquid ($\chi_{\mathrm{GaCl_3}} = 0.50$), and of the less active $AlCl_3$, have also been studied.

The inactive mixture of [C_4mim]Cl–$GaCl_3$, $\chi_{\mathrm{GaCl_3}} = 0.50$, and hydrogen peroxide was biphasic, comprising an aqueous phase and an organic phase. In the organic phase, the only detected gallium(III) species was the neutral tetrachlorogallate(III) anion, confirmed by the presence of a Raman Ga–Cl stretching frequency at 349 cm^{-1} (Fig. 2A),[32] and a narrow ^{71}Ga NMR signal at 250 ppm (Fig. 2B),[19] both characteristic of the tetrahedral $[GaCl_4]^-$. The aqueous phase contained H_2O_2 (Raman O–O stretching frequency at 876 cm^{-1}, Fig. 2A), and the product of complete hydrolysis of the chlorogallate(III) anion, $[Ga(H_2O)_6]^{3+}$, characterised by a narrow ^{71}Ga NMR signal at 0 ppm (Fig. 2B), as the only observable gallium species.

The mixture of $AlCl_3$ and hydrogen peroxide formed a homogenous liquid, in a very exothermic mixing process. It contained products of $AlCl_3$ hydrolysis, but no H_2O_2. Hydrogen peroxide was assumed to have undergone a rapid decomposition due to temperature and/or released HCl, which may be the main factor lowering the activity of $AlCl_3$.

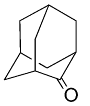
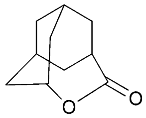
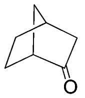
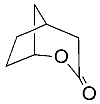
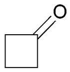
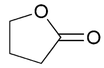
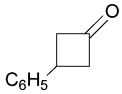
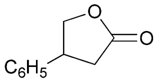
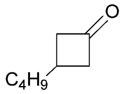
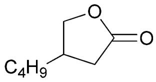
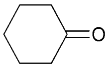
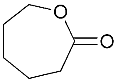
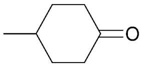
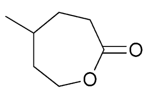
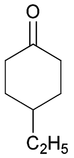
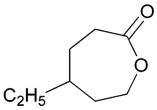
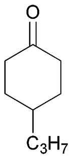
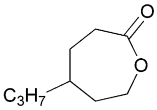
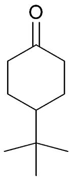
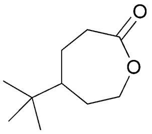
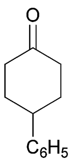
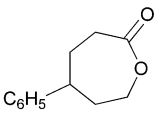
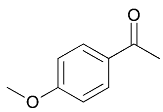
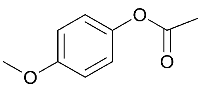
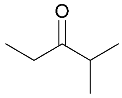
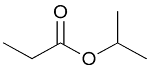
The catalytically active ionic liquid, [C_4mim]Cl–$GaCl_3$ ($\chi_{\mathrm{GaCl_3}} = 0.75$), in its neat state, contained oligonuclear chlorogallate(III) anions, such as $[Ga_2Cl_7]^-$ and $[Ga_3Cl_{10}]^-$, as indicated by a group of Raman signals between 500 and 100 cm^{-1} (Fig. 3A), that correspond to vibrations of terminal and bridging chlorides in oligomeric chlorogallate(III) anions, in agreement with the literature.[33]

Upon the addition of the ionic liquid to aqueous hydrogen peroxide, a single phase was formed in a highly exothermic process. The same was observed upon the addition of solid $GaCl_3$ to aqueous H_2O_2. For both solutions, Raman spectra exhibited a Ga–Cl stretching frequency at 348 cm^{-1}, corresponding to monomeric chlorogallate(III) units, and signal at 876 cm^{-1}, corresponding to the O–O stretch in H_2O_2 (Fig. 3A). The ^{71}Ga NMR spectra both contained two signals (Fig. 3B). A broad peak *ca.* 240 ppm corresponded to tetracoordinate gallium(III) anions. The broadening and a slight upfield shift compared to that for $[GaCl_4]^-$ may suggests the partial replacement of a chloride with a hydroxide ligand (^{71}Ga NMR signal for $[GaOH_4]^-$ is at 225 ppm).[34] It may also indicate the



Scheme 2 Electrophilic activation of (a) ketone by Lewis acid, (b) the intermediate by Lewis acid, and (c) ketone by Brønsted acid in Baeyer–Villiger oxidation with hydrogen peroxide. Adapted from ref. 2.

Table 5 Oxidation of selected cyclic ketones to lactones[a]

Entry	Ketone	Lactone	Time/min	Yield[b]/%
1			1	99 (94)
2			5	99 (90)
3			1	99 (92)
4			1	99 (93)
5			1	99 (89)
6			1	26
7			30	99 (91)
8			30	99 (90)
9			15	99 (93)
10			15	99 (92)
11			120	99 (91)
12			120 240	15 15
13			120	50

[a] Reaction conditions: ketone (1.34 mmol), 30% aq. H_2O_2 (2.68 mmol), $[C_4mim]Cl–GaCl_3$, $\chi_{GaCl_3} = 0.75$ (1.34 mmol), RT. [b] Yields determined using GC, isolated yields given in parenthesis.

exchange with other gallium species. The signal at 0 ppm was assigned to $[Ga(H_2O)_6]^{3+}$, but again – the broadening indicates exchange with other species. These results are in agreement with prior NMR studies on $GaCl_3$ hydrolysis.[33,34] In addition, complementary FAB-MS studies on hydrolysis of chlorogallate(III) ionic liquids revealed that the hydrolysis proceeds *via* chlorohydroxygallate(III) anions, such as $[GaCl_3(OH)]^-$ and $[GaCl(OH)_3]^-$,[35] which is in agreement with observed here small upfield shift in the ^{71}Ga NMR spectrum.

In summary, both catalytically active systems contain mixtures of $[GaCl_4]^-$, chlorohydroxygallate(III) anions, and $[Ga(H_2O)_6]^{3+}$, coexisting in the same phase with H_2O_2. The monomeric $[GaCl_4]^-$ anion it is not known to either undergo facile chloride replacement, or to expand its coordination to accommodate a fifth ligand; therefore it is commonly described as 'neutral', as opposed to 'Lewis acidic'.[27] In contrast, chlorohydroxygallate(III) anions, such as $[GaCl_3(OH)]^-$, are less sterically crowded and have been demonstrated to expand to penta- or hexacoordinate motif in the presence of O-donors, L, *e.g.* $\{GaCl_3L_2\}$.[36] Therefore, chlorohydroxygallate(III) complexes are proposed to be the active Lewis acidic species in BV oxidation (Scheme 2a and b), which also explains the beneficial influence of water in this reaction. Finally, a very slow conversion of ketone to lactone (43% after 5 h) detected in the presence of the 'inactive' $[C_4mim]Cl–GaCl_3$ ($\chi_{GaCl_3} = 0.50$), was probably caused by hydrolytically-generated HCl, protonating the ketone and resulting in its mild activation (Scheme 2c).[2]

Substrate scope

To determine the catalytic potential of the chlorogallate(III) ionic liquid, $[C_4mim]Cl–GaCl_3$ ($\chi_{GaCl_3} = 0.75$), it was used as a catalyst for the synthesis of a range of lactones from the corresponding ketones (Table 5). Numerous cyclic ketones were readily oxidised to the corresponding lactones in high yields (93–99%) under the optimised reaction conditions, which were in general remarkably better than those reported in the literature.[4–7]

Very reactive, strained cyclobutanones were oxidised to γ-butyrolactones in 1 min with 99% yield. High yields and short reaction times were also achieved for the oxidation of 2-adamantanone and norcamphor. Non-strained cyclohexanones, which are much less reactive, were also successfully oxidised to corresponding ε-caprolactones at 99% yields. Reaction times varied from 15 to 120 min, depending on the substituent in the *para* position. The only exception was unsubstituted cyclohexanone, which yielded only 26% of ε-caprolactone after 1 min with full conversion of ketone. This anomaly could be caused by the presence of Brønsted acidic protons, which are known to convert cyclohexanone to the polymeric peroxides in the presence of H_2O_2.[2,37] Unfortunately, isopropyl propanoate and *p*-methoxyphenyl acetate, which are reactive representatives of linear ketones, were slowly oxidise and did not reached the full conversion.

Conclusions

The gallium(III) chloride systems provide the fastest known homogenous activation of the Baeyer–Villiger oxidation with aqueous hydrogen peroxide to produce near quantitative yields (89–94%) of lactones.[2] Gallium(III) chloride was found to be a very active catalyst, especially in aprotic solvents. Lewis acidic chlorogallate(III) ionic liquids were also extremely active, and in addition allowed for the elimination of volatile molecular solvents.

It was demonstrated that water was crucial for the efficient process activation. The active species, postulated based on Raman and ^{71}Ga NMR spectroscopies, were hydroxychlorogallate(III) anions, such as $[GaCl_3(OH)]^-$ or $[GaCl(OH)_3]^-$, which are the intermediate products of hydrolysis of both $GaCl_3$ and chlorogallate(III) anions.

Acknowledgements

This work was financed by the Polish Ministry of Science and Higher Education, National Science Centre (grant no. UMO-2012/06/M/ST8/00030). MM would like to acknowledge the COST Action (CM1206 EXIL – Exchange on Ionic Liquids), which allowed for the Short Term Scientific Mission in The QUILL Research Centre.

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