Removal of Oxide Contamination from Ambient-temperature Chloroaluminate(III) Ionic Liquids

Ala'a K. Abdul-Sada,[a] Anthony G. Avent,[a] Michael J. Parkington,[a] T. Anthony Ryan,[b] Kenneth R. Seddon[c] and Thomas Welton[d]
[a] *School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, UK*
[b] *ICI Chemicals and Polymers Ltd., P.O. Box 8, The Heath, Runcorn WA7 4QD, UK*
[c] *School of Chemistry, David Keir Building, The Queen's University of Belfast, Belfast BT9 5AG, UK*
[d] *Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, UK*

Treatment of ambient-temperature chloroaluminate(III) ionic liquids with phosgene results in the removal of oxide impurities in the form of carbon dioxide; the reaction was investigated using multinuclear NMR (^{13}C and ^{17}O) spectroscopy and mass spectrometry. Both the CO_2 and the excess of phosgene are removed *in vacuo* to leave the ionic liquid free from oxide contamination.

Ambient-temperature ionic liquids formed by mixtures of organic chloride salts and aluminium(III) chloride have traditionally been considered as aprotic, anhydrous systems. However, it is well known that the bridged hydrido species $[Mo_2Cl_8H]^{3-}$ is formed when $[Mo_2Cl_8]^{4-}$ salts are added to acidic ionic liquids,[1] and that when $[TiCl_6]^{2-}$ salts are dissolved in basic ionic liquids, $[TiOCl_4]^{2-}$ ions are formed.[2] These ions are generated by reactions with proton and oxide contaminants respectively, which, unless specific action is taken to remove them, are ubiquitously present in the ionic liquids.[3,4] The removal of proton impurities from the ionic liquids has been achieved using ethylaluminium dichloride.[5] This paper gives a full account of the removal of oxide contamination from 1-ethyl-3-methylimidazolium chloride-aluminium(III) chloride ([emim]Cl-$AlCl_3$) ionic liquids, and contains the essential experimental details omitted from our preliminary communication.[6]

Experimental

Handling Phosgene.—Phosgene is a toxic gas, with a permissible UK occupational exposure limit of 0.4 mg m^{-3} of air (0.1 ppm v/v).[7] In the event of exposure, the victim may experience chest pain, coughing and rapid breathing associated with pulmonary œdema, and it may take over 24 h for symptoms to appear. There is no antidote to phosgene poisoning,[8] and hence treatment is usually directed to the main symptom toxic pulmonary œdema.[9] Hence, all manipulations involving phosgene were carried out in a well ventilated fume cupboard with a face velocity of >0.75 m s^{-1}, and in the presence of at least one other experienced research worker. The atmosphere both inside and outside the fume cupboard was constantly checked using Dräger tubes[10] and detector tape (Rimon Laboratories Ltd.). All glassware used greaseless taps, and joints were lubricated with Teflon sleeves. After use, the phosgene was destroyed by passage through a column containing moist activated charcoal. The fume cupboard was fitted with an alarm system, which was activated automatically if the extractor mechanism of the fume cupboard failed, or manually in the event of an accident. After use, all equipment was washed with an aqueous solution of sodium hydroxide before removal from the fume cupboard.

Spectroscopic Measurements.—The ^{13}C and ^{17}O NMR spectra were recorded on a Bruker WM360 NMR spectrometer operating at 90.55 and 48.82 MHz, respectively. Mass spectra were recorded on a Kratos MS80RF mass spectrometer.

Preparation of the [emim]Cl–$AlCl_3$ *Ionic Liquids.*—The preparation of the ionic liquids was as previously described.[4]

Phosgene in Basic [$X(AlCl_3) = 0.45$] *Ionic Liquid* (*X = mole fraction*).—Phosgene (0.52 g, 5.3 mmol) was condensed into an NMR tube (8 mm diameter) containing a basic ionic liquid (1.93 g, 7.58 mmol). The tube was sealed *in vacuo*, and the ^{13}C-$\{^1H\}$ and ^{17}O NMR spectra were recorded.

Phosgene in Acidic [$X(AlCl_3) = 0.55$] *Ionic Liquid.*—Phosgene (0.48 g, 4.9 mmol) was condensed into an NMR tube (8 mm diameter) containing an acidic ionic liquid (2.03 g, 6.56 mmol). The tube was sealed *in vacuo*, and the ^{13}C-$\{^1H\}$ and ^{17}O NMR spectra of the contents were recorded.

Phosgene in Basic [$X(AlCl_3) = 0.45$] *Ionic Liquid with Added* $^{17}OH_2$.—An amount of $^{17}OH_2$ (0.007 cm^3, 0.39 mmol, 50% ^{17}O enriched) was added slowly, using a micro-syringe, to an NMR tube containing basic ionic liquid (2.19 g, 8.56 mmol). White strands of solid immediately formed, in an exothermic reaction, which were dissolved by heating the tube to 70 °C for 5 min. The ^{17}O NMR spectrum was then recorded. The contents of the tube were transferred to a second NMR tube fitted with a greaseless tap and a ground-glass joint inside a high integrity dry-box. The tube was transferred to a vacuum line and $COCl_2$ (0.54 g, 5.5 mmol) was condensed into the tube. The NMR tube was sealed *in vacuo* and the ^{13}C-$\{^1H\}$ and ^{17}O NMR spectra were recorded. The tube was then attached to the vacuum line *via* Portex tubing, opened, and the volatile components condensed into an adjacent ampoule. The electron-impact mass spectrum of the contents of the ampoule was recorded. The NMR tube was continuously evacuated at 100 °C for 12 h, to ensure the complete removal of all of the volatile material. The tube was then resealed *in vacuo*, and the ^{13}C-$\{^1H\}$ and ^{17}O NMR spectra were again recorded.

Phosgene in Acidic [$X(AlCl_3) = 0.55$] *Ionic Liquids with Added* $^{17}OH_2$.—An amount of $^{17}OH_2$ (0.007 cm^3, 0.39 mmol, 50% ^{17}O enriched) was added slowly to an NMR tube (8 mm diameter) containing acidic ionic liquid. A vigorous exothermic reaction ensued and the ^{17}O NMR spectrum was recorded. The contents of the tube were transferred to a second NMR tube fitted with a ground-glass joint and a greaseless tap. The tube was transferred to the vacuum line and $COCl_2$ (0.52 g, 5.3 mmol) was condensed into the tube. The contents of the NMR tube were allowed to mix intimately (*ca.* 1 min) before all of the volatile components were removed *in vacuo* (*ca.* 12 h). The NMR tube was sealed *in vacuo*, and the ^{17}O NMR spectrum of its contents recorded.

Results and Discussion

The spectra presented here contain signals which may be attributed to the ionic liquid itself and impurities in the system. As the NMR spectra (^1H, ^{13}C and ^{27}Al) of the [emim]Cl-$AlCl_3$ ionic liquids have been discussed elsewhere,[11-13] only those signals which arise from solutes and impurities will be discussed here.

Phosgene in Basic Ionic Liquid.—The ^{13}C NMR spectrum of the neat ionic liquid is contrasted with that of the ionic liquid after the addition of phosgene in Fig. 1. The spectrum of the ionic liquid with added $COCl_2$ shows two new peaks. That at δ 144.6 (A) can be attributed to $COCl_2$ (*cf.* δ 142.8 for $COCl_2$ in CD_2Cl_2) and the weak shoulder at δ 124.3 (B) to CO_2 (*cf.* δ 124.2 for CO_2 gas[14]).

The ^{17}O NMR spectrum of the basic ionic liquid with added phosgene (Fig. 2) shows two peaks at δ 497.5 and 84.0 due to $COCl_2$ and CO_2, respectively (*cf.* δ 483.6 for $COCl_2$ in CD_2Cl_2 and δ 64.5 for CO_2 gas[15]). The ^{17}O NMR spectrum of the neat ionic liquid showed no discernible peaks in a noisy spectrum.

The presence of peaks attributable to CO_2 in both the ^{13}C and ^{17}O NMR spectra of the basic ionic liquid with added phosgene indicates that the phosgene has reacted with oxide impurities in the ionic liquid to produce CO_2. However, although the phosgene used was free of CO_2, the adventitious presence of CO_2 could not be excluded as a possibility. Therefore, $^{17}OH_2$ was added to the basic ionic liquid to demonstrate conclusively that the CO_2 produced was generated from the reaction of $COCl_2$ with oxide containing impurities in the ionic liquid. The quantity of $^{17}OH_2$ added gave a mole ratio of ^{17}O:Al of *ca.* 1:20. The ^{17}O NMR spectra, recorded at 283 and 343 K (Fig. 3), of the $^{17}OH_2$ contaminated basic ionic liquid showed very broad peaks (δ 69.8 for the spectrum recorded at 343 K). In addition, the spectrum at 343 K showed a discernible shoulder (δ ≈ 56). The high-temperature spectrum clearly shows that there is more than one oxygen-containing species present in the basic ionic liquid. This is in accord with

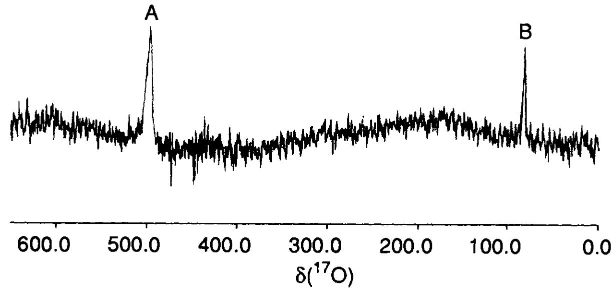

Fig. 2 The ^{17}O NMR spectrum (48.82 MHz; 273 K) of basic ionic liquid with added phosgene (A = $COCl_2$ and B = CO_2)

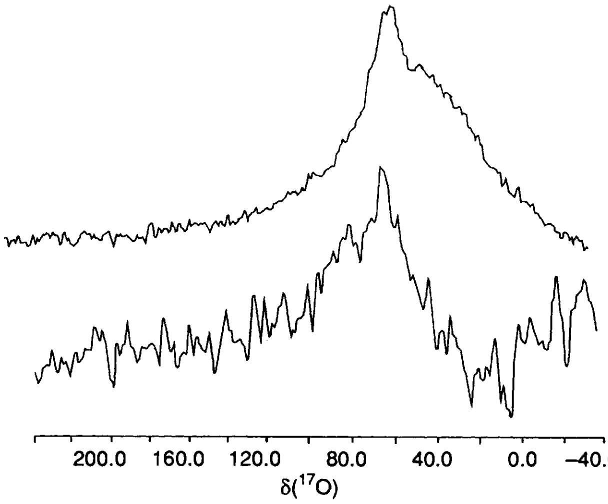

Fig. 3 The ^{17}O NMR (48.82 MHz) spectra of basic ionic liquid with added $^{17}OH_2$ at (lower) 283 and (upper) 343 K

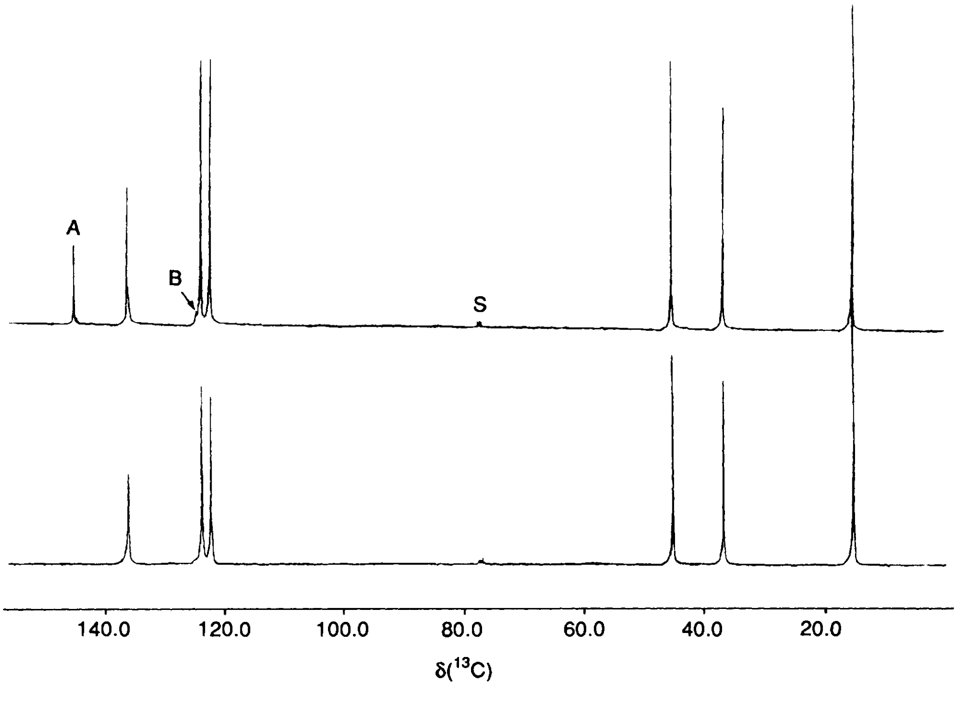

Fig. 1 The ^{13}C NMR spectra (90.55 MHz; 273 K) of (lower) basic ionic liquid and (upper) with added phosgene (A = $COCl_2$, B = CO_2 and S = $CDCl_3$)

the conclusions drawn from the room-temperature spectra of [emim]Cl–$AlCl_3$ ionic liquids contaminated with varying amounts of $^{17}OH_2$.[16]

The ^{13}C NMR spectrum of the $^{17}OH_2$ contaminated ionic liquid after the addition of phosgene (Fig. 4) showed peaks at δ 144.4 and 124.2 due to $COCl_2$ and CO_2[14] respectively. However, the ^{17}O NMR spectrum (Fig. 5) showed only one peak at δ 79.1 due to CO_2;[15] no peak due to $COCl_2$ was observed. Clearly, ^{17}O labelled CO_2 had been generated.

The mass spectrum of the product gases showed peaks at *m/z* (ion, relative intensity) = 44 ($[C^{16}O_2]^+$, 100), 45 ($[C^{17}O^{16}O]^+$, 78) and 46 ($[C^{17}O_2]^+$, 72). No ion due to $C^{17}OCl_2$ at *m/z* = 99 was observed. The presence of all possible isotopomers of CO_2 is consistent with an equilibrium between CO_2 and $[CO_3]^{2-}$, equation (1), as is suggested by the known procedure for the intentioned introduction of oxide to ionic liquids with $Li_2[CO_3]$, equation (2).[17]

$$C^{17}O^{16}O + {}^{17}O^{2-} \rightleftharpoons [C^{17}O_2{}^{16}O]^{2-} \rightleftharpoons C^{17}O_2 + {}^{16}O^{2-} \quad (1)$$

$$O^{2-} + CO_2 \rightleftharpoons [CO_3]^{2-} \quad (2)$$

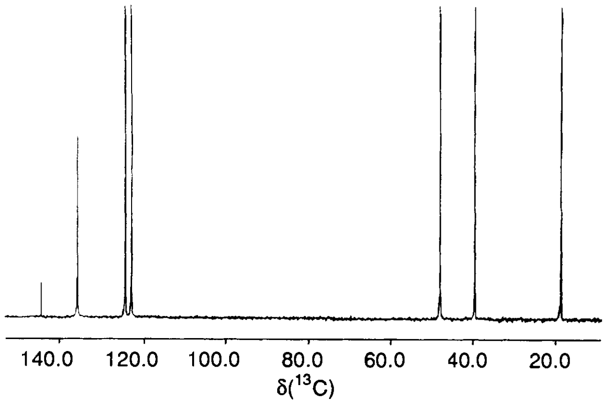

Fig. 4 The ^{13}C NMR spectrum (90.55 MHz; 273 K) of $^{17}OH_2$ contaminated basic ionic liquid after addition of phosgene

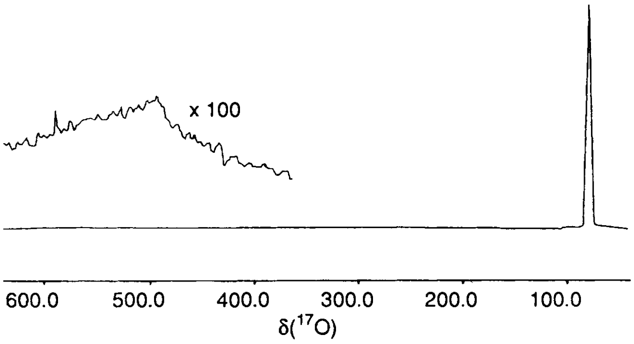

Fig. 5 The ^{17}O NMR spectrum (48.82 MHz; 273 K) of $^{17}OH_2$ contaminated basic ionic liquid after addition of phosgene

The ^{17}O NMR spectrum of the basic ionic liquid, after removal of all of the volatile components, showed no peaks due to oxide ion impurities, $COCl_2$ or CO_2. Hence, the method was demonstrated to have successfully removed all oxide impurity and left an ionic liquid with no new contaminants. The reaction of phosgene with the nominal impurity of the ionic liquids, '$AlOCl_2^-$', can now be summarized as equation (3).

$$\text{'}AlOCl_2^{-}\text{'} + COCl_2 \longrightarrow [AlCl_4]^- + CO_2 \quad (3)$$

The reaction of phosgene with main group metal oxides to generate metal chlorides and carbon dioxide has been known since the nineteenth century, and is reviewed in detail elsewhere.[18] The thermodynamic driving force is the elimination of carbon dioxide.

Phosgene in Acidic Ionic Liquid.—The ^{13}C NMR spectrum of the neat acidic ionic liquid is contrasted with that of the ionic liquid after the addition of phosgene in Fig. 6. As with the basic ionic liquid, the spectrum of the acidic ionic liquid with added phosgene showed peaks due to $COCl_2$ at δ 146.2 (*cf.* δ 142.8 for $COCl_2$ in CD_2Cl_2) and CO_2 at δ 124.1 (*cf.* δ 124.2 for CO_2 gas[14]). The ^{17}O NMR spectrum of the acidic ionic liquid after the addition of phosgene (Fig. 7) also showed peaks attributable to $COCl_2$ at δ 479.6 (*cf.* δ 483.6 for $COCl_2$ in CD_2Cl_2) and CO_2 at δ 66.7 (*cf.* δ 64.5 for CO_2 gas[15]).

The results demonstrate that the action of phosgene in acidic ionic liquids, as in basic ionic liquids, is to form CO_2 by reaction with oxide-containing impurities in the ionic liquid. To ensure that the complete removal of oxide ion could be achieved from all compositions of the ionic liquid, $^{17}OH_2$ was added to the acidic ionic liquid.

The ^{17}O NMR spectrum of the acidic ionic liquid (Fig. 8) showed two signals at δ 54.2 and 99.6, in general agreement with the results of Zawodzinski and Osteryoung.[16] After treatment with phosgene and removal of all of the volatile components, the ^{17}O NMR spectrum of the ionic liquid showed no peaks due to the oxide impurities, $COCl_2$ or CO_2.

Summary.—Clearly, the removal of oxide contamination has been achieved from both basic and acidic compositions of the

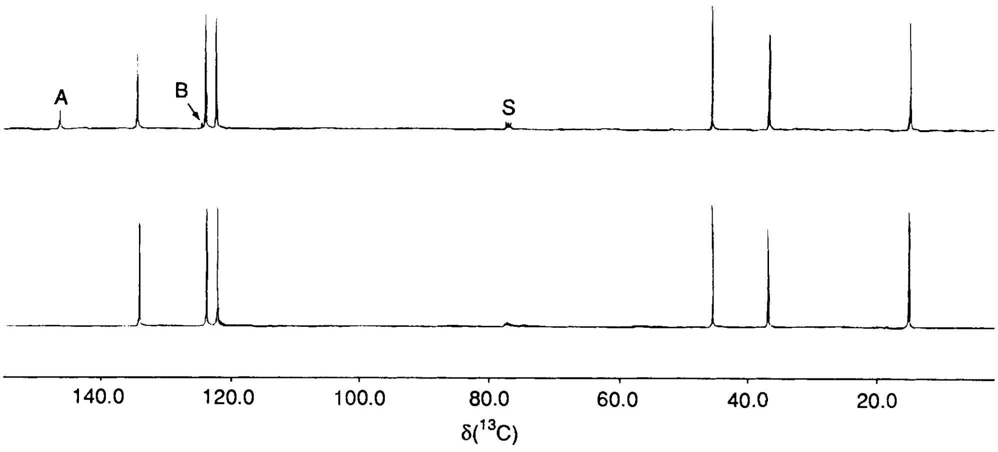

Fig. 6 The ^{13}C NMR spectra (90.55 MHz; 273 K) of (lower) acidic ionic liquid and (upper) with added phosgene (A = $COCl_2$, B = CO_2 and S = $CDCl_3$)

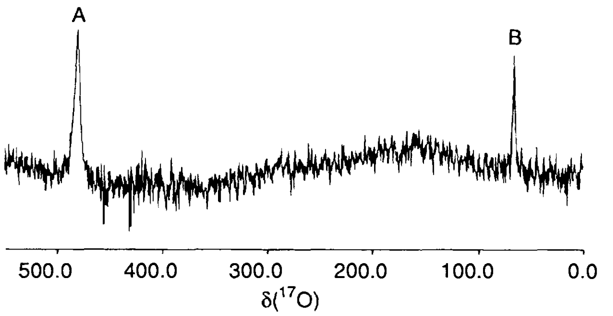

Fig. 7 The ^{17}O NMR spectrum (48.82 MHz; 273 K) of acidic ionic liquid with added phosgene (A = $COCl_2$ and B = CO_2)

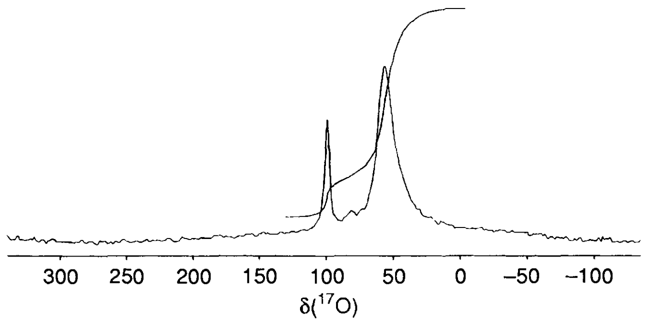

Fig. 8 The ^{17}O NMR spectrum of $^{17}OH_2$ contaminated acidic ionic liquid

[emim]Cl–$AlCl_3$ ionic liquids. Since the preliminary publication of these results,[6] this method has become widely adopted for the removal of oxide contamination from the ionic liquids,[19,20] and the conversion of oxide chloride complexes dissolved in ionic liquids into chloride complexes [*e.g.* equation (4)].[21] Also, it has been used to purify high-temperature

$$[NbOCl_5]^{2-} + COCl_2 \longrightarrow [NbCl_6]^- + Cl^- + CO_2 \quad (4)$$

chloroaluminate(III) ionic liquids.[22] It is now a well established and well proven technique, and we would encourage all workers in the field to adopt it as a routine procedure.

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