The Removal of Oxide Impurities from Room Temperature Halogenoaluminate Ionic Liquids

Ala'a K. Abdul-Sada,[a] Anthony G. Avent,[a] Michael J. Parkington,[a] T. Anthony Ryan,[b] Kenneth R. Seddon,[a] and Thomas Welton[a]

[a] *School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, U.K.*
[b] *Polymer Chemistry Group, ICI Chemicals and Polymers Group, P.O. Box 8, The Heath, Runcorn, Cheshire WA7 4QD, U.K.*

Treatment of room-temperature halogenoaluminate ionic liquids {*e.g.* $AlCl_3$–[MeEtim]Cl; $[MeEtim]^+$ = 1-methyl-3-ethylimidazolium cation} with phosgene ($COCl_2$) results in the removal of oxide impurities in the form of carbon dioxide.

Room-temperature halogenoaluminate ionic liquids {*e.g.* $AlCl_3$–[MeEtim]Cl or $AlCl_3$–[*N*Bupy]Cl; $[MeEtim]^+$ = 1-methyl-3-ethylimidazolium cation, $[NBupy]^+$ = 1-butylpyridinium cation} have been the subject of much recent attention.[1,2] In addition to their remarkable liquid range and excellent solvent properties, they have wide and convenient electrochemical and spectroscopic windows, and they are being increasingly used as solvents for studying metal chloride complexes by a wide range of physical techniques. One factor which is currently hampering the wider use of these solvents is the ubiquitous presence of oxide ion impurities, often referred to as '$AlOCl_2^-$' for convenience (although no evidence for such a species exists), which are recognized as a problem both in room-temperature ionic liquids[3,4] and in high-temperature melts.[5] These impurities will transfer oxide ion to solutes with a high oxygen affinity [such as titanium(IV), see equation (1)],[3,4] and severely inhibit studies of such systems.

$$[TiCl_6]^{2-} + \text{'}AlOCl_2^-\text{'} \rightleftharpoons [TiOCl_4]^{2-} + [AlCl_4]^- \quad (1)$$

It has been known for many years that phosgene, $COCl_2$, will react with metal oxides and oxide ions according to equation (2).[6] Accordingly, we passed CO_2-free phosgene† through a basic‡ $AlCl_3$–[MeEtim]Cl ionic liquid (2 cm^3), prepared by the normal method, with rigorous exclusion of water.[7] The ^{13}C and ^{17}O n.m.r. spectra of the resulting solution showed, in addition to phosgene, the presence of dissolved carbon dioxide. In a separate experiment, we added 7 μl of $^{17}OH_2$ to the basic $AlCl_3$–[MeEtim]Cl ionic liquid, and then treated this with phosgene. Although the ^{13}C n.m.r. spectrum of this treated solution was similar to that obtained in the first experiment, the ^{17}O n.m.r. spectrum showed a

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† **Caution.** All operations conducted with phosgene must be performed in a well ventilated fume cupboard.

‡ A basic ionic liquid contains a molar excess of [MeEtim]X over aluminium(III) halide; an acidic ionic liquid contains a molar excess of aluminium(III) halide over [MeEtim]X.[1]

tremendously enhanced signal due to carbon dioxide. Furthermore, when the product gas was removed *in vacuo* and analysed by mass spectrometry, it was found to be predominantly $C^{17}O^{16}O$, with significant amounts of $C^{16}O_2$ and $C^{17}O_2$ also present, indicating that equilibria (3) are established readily under ambient conditions (*n.b.* lithium carbonate is known to be an oxide ion donor under these conditions).[4] No $C^{17}OCl_2$ was detected. Similar results were obtained when acidic compositions were studied. Thus, using the normal conventions of ionic liquids, equation (4) represents the overall reaction between phosgene and the oxide-containing impurities. Both the reagent and the product are gaseous, and can be removed from the liquid by continuous evacuation at room temperature. It is expected that carbonyl dibromide, $COBr_2$, will produce a comparable effect on bromide based-ionic liquids {*e.g.* $AlBr_3$–[MeEtim]Br}.[8]

$$O^{2-} + COCl_2 \longrightarrow CO_2 + 2Cl^- \quad (2)$$

$$C^{17}O^{16}O + {}^{17}O^{2-} \rightleftharpoons [C^{17}O_2{}^{16}O]^{2-} \rightleftharpoons C^{17}O_2 + {}^{16}O^{2-} \quad (3)$$

$$COCl_2 + \text{'}AlOCl_2{}^{-}\text{'} \longrightarrow CO_2 + [AlCl_4]^- \quad (4)$$

We thank the S.E.R.C and I.C.I. for a CASE studentship (to M. J. P.) and financial support, the S.E.R.C. for a postgraduate award (T. W.), and the Iraqi government for a scholarship (A. K. A.-S.).

Received, 29th May 1987; Com. 737

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