

Ionic liquids of superior thermal stability

Cody G. Cassity,^a Arsalan Mirjafari,^b Katie J. Strickland,^a and James H. Davis, Jr.*^a

Supporting Information

^a Department of Chemistry, The University of South Alabama

^b Department of Chemistry and Mathematics, Florida Gulf Coast University

Calibration of heat stage display *T* vs. content *T*

New porcelain crucibles were charged with samples of elemental tin ($T_m = 231.9\text{ }^\circ\text{C}$), bismuth ($T_m = 271.4\text{ }^\circ\text{C}$), and lead ($T_m = 327.5\text{ }^\circ\text{C}$). These were placed on the heat stage of a Torrey Pines Scientific EchoTherm HS-30 digital heater (Specifications can be found at: <http://www.torrey-pines.com/products/digital-hot-plates/echotherm-hp30-and-hs30>). The stage temperature was ramped to $225\text{ }^\circ\text{C}$ over a period of 1 h. Then, it was manually increased in $5\text{ }^\circ\text{C}$ increments, while monitoring the contents of the crucibles. Once a standard melted, the stage temperature was noted, and the known versus apparent melting temperatures compared. In all cases, the display *T* at which the given standard melted was ca. $75\text{ }^\circ\text{C}$ ($\pm 5\text{ }^\circ\text{C}$) greater than the known melting point of the material.

Comment on the Charette Synthesis Approach

In our initial attempts to reproduce the Charette synthesis of various tetraarylphosphonium salts, our outcomes and yields were highly erratic. Thanks to an exchange of emails with Charette (Department of Chemistry, Université de Montréal), we learned that our problem was one of temperature control with respect to the reaction. In our hands, as in Charette's, the reaction tends to work only within a very narrow temperature range – $180\text{ }^\circ\text{C}$ to $190\text{ }^\circ\text{C}$. However, we found it exceedingly difficult to control the temperature of the reaction system using a conventional heater-stirrer. Our best results were obtained when using a TorreyPines Scientific HS-30 device to provide stirring and precise temperature control. Interestingly, in all cases a successful outcome is signaled by a colour change of the reaction solution to an intense emerald green, which is likely the nickel-based catalytic intermediate of the reaction.

Further observations and comments on the apparent polymerization of **2**

Judging from integrated peak intensities in both the ^1H - and ^{31}P -NMR spectra of **2**, about one-third of the cations in the 48 h stressed sample of **2** were altered, likely explaining the failure of this salt to recrystallize as it cooled. Its ^{31}P spectrum was especially telling in that along with a peak for unchanged **2**, new ones (one major and several smaller) were observed, but all of these are at chemical shifts (around 24 ppm) consistent with phosphonium ions; there was no evidence of aryl ring cleavage from the P center, which would result in the formation of clearly distinguishable phosphine oxides. Then, in the ^1H -spectrum, the expected CH_3 peak for unaltered **2** was present, but was complimented by a broad new peak nearby (2.23 ppm). After 96 hours, the overwhelming majority of the sample (judging from both the ^1H - and ^{31}P -spectra) had converted into the new species. Both the chemical shift position and the broadness of the 2.23 ppm peak are suggestive of CH_2 groups linking aromatic rings in polymers. On this basis, we hypothesize that oligomerization has occurred (with the exo-core CH_3 groups becoming CH_2 groups linking the cations) in the stressed sample of **2**. We anticipate follow-on work to further investigate this possibility, since (if borne out by additional data) such high-T stable ionomers would be of considerable interest in their own right.

Thermal stability as a function of crucible material

Other investigators have reached different conclusions with regard to the thermal stability of ILs as a function of the material from which the experimental container is made (See, for example, References 2a and 2b in the main manuscript). We revisited the issue with salt **1**. In a side-by-side comparison, samples of **1** were heated at 425 °C (stage *T*) in platinum and porcelain crucibles. In the former, 0.8% mass loss was observed. In contrast, the sample in the porcelain vessel lost 2.3% of its initial mass. It is also worth noting that, during the heating period, the molten IL exhibited a pronounced tendency to creep upward and wet the walls of the porcelain vessel, while little activity was noticed in the platinum vessel.

NMR Data, ILs 1-5

All spectra acquired using a JEOL YH-500 (500 MHz), in CDCl₃ using standard nuclei-appropriate frequencies.

IL 1

³¹P (ppm): 28.87, singlet.

¹H (ppm): 7.61, m, 8H; 7.77, m, 8H; 7.90, m, 4H.

¹³C (ppm): 117.43, d; 119.87, q (CF₃); 130.69, d; 134.32, d; 135.73, d.

IL 2

³¹P (ppm): 23.63, singlet.

¹H (ppm): 2.53, s, 3H (CH₃); 1.28, m, 2H; 7.53-7.63, m, 8H; 7.77, m, 6H; 7.88, m, 3H.

¹³C (ppm): 21.85, s, CH₃; 113.60, d; 117.80, d; 119.87, q (CF₃); 130.60, d; 131.45, d; 134.26, d; 135.60, d; 147.43, d.

IL 3

³¹P (ppm): 22.74, s.

¹H (ppm): 3.95, s, 3H, OCH₃; 7.04-7.28, m, 4H; 7.45-7.92, m, 15H.

¹³C (ppm): 55.92, s, CH₃; 119.80, d; 119.87, q, CF₃; 120.15, d; 130.11, d; 130.33, d; 134.18, d; 134.88, s; 136.07, d; 171.48.

IL 4

^{31}P (ppm): 15.64, singlet.

^1H (ppm): 7.39, m, 1H; 7.61, m, 6H; 7.75, m, 6H; 7.89, m, 4H; 8.00, m, 1H.

^{13}C (ppm): 116.61, d; 118.22, d; 119.87, q (CF_3); 129.89, d; 130.69, d; 131.80, d; 133.88, d; 135.73, d; 141.90, d.

IL 5

^{31}P (ppm): 23.25, singlet.

^1H (ppm): 7.10-7.36, m, 5H; 7.40-7.55, m, 4H; 7.57-7.70, m, 6H; 7.75, m, 6H; 7.87, m, 3H.

^{13}C (ppm): 108.84, d; 117.48, s; 118.35, d; 119.87, q (CF_3); 120.85, s; 125.86, s; 130.40, s; 130.58, d; 134.20, d; 135.68, d; 136.48, d; 153.70, s; 164.35, s.