Supplementary information for:
Esterification in ionic liquids: the influence of solvent basicity

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Experimental Section

Materials and Reagents All reagents were purchased from common commercial suppliers. Unless otherwise stated, solvents and reagents were freshly distilled and dried using standard procedures.

Analytical Procedures. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm (versus tetramethylsilane) and coupling constants in Hz. FAB mass spectra were recorded using a magnetic sector mass spectrometer of EBE configuration.

All ^1H and ^{13}C NMR assignments for ionic liquid characterization based on those reported in the literature (Welton *et al.*, T. *Phys. Chem. Chem. Phys.* **2001**, 3, 5192-5200).

Synthesis of 1-butyl-1-methylimidazolium chloride [$\text{C}_4\text{C}_1\text{im}$] Cl A flask containing 1-methylimidazole (120 mL, 1.50 mols) and EtOAc (100 mL) was cooled in an ice bath and 1-chlorobutane (200 mL, 1.92 mols) was added, drop-wise under N_2 . The solution was allowed to reach room temperature and then heated at 45 °C, with stirring, for 14 days. The two phase mixture was placed in the freezer for 2 days and the EtOAc was carefully decanted from the solid white product which was washed with EtOAc (3×30 mL), then dried *in vacuo* for 1 hr. The powdery white crystals were washed again with EtOAc (3×30 mL) and dried *in vacuo* for 7 hrs, affording [$\text{C}_4\text{C}_1\text{im}$] Cl as a completely white, crystalline solid (120 g, 46%).

δ_{H} : (400 MHz, $\text{DMSO}-d^6$) / ppm 9.47 (1H, s, N_2CH), 7.86 (1H, s, NCH), 7.78 (1H, s, NCH), 4.19 (2H, t, $^3J = 7.1$ Hz, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 3.87 (3H, s, NCH_3), 1.76 (2H, quintet, $^3J = 7.3$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.25 (2H, sextet, $^3J = 7.1$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), and 0.89 (3H, t, $^3J = 7.3$ Hz, $\text{N}(\text{CH}_2)_3\text{CH}_3$).

δ_{C} : (100 MHz, $\text{DMSO}-d^6$) / ppm 136.8 (s, N_2CH), 123.4 and 122.2 (s, 2NCH), 48.2 (s, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 35.6 (s, NCH_3), 31.3 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.6 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), and 13.3 (s, $\text{N}(\text{CH}_2)_3\text{CH}_3$).

m/z (FAB+): 313 ($[(\text{C}_4\text{C}_1\text{im})_2\text{Cl}]^+$, 22%) and 139 ($[\text{C}_4\text{C}_1\text{im}]^+$, 100%)

m/z (FAB-): 188 ([matrix + Cl] $^-$)

Elemental Analysis (predicted): %C = 55.14 (55.01), %H = 8.74 (8.66) and %N = 15.72 (16.04)

Remaining syntheses as previously reported:

Synthesis of N-butyl-N-methylpyrrolidinium chloride, [$\text{C}_4\text{C}_1\text{py}$] Cl To a mixture of 1-methyl pyrrolidine (200 mL, 1.92 mol) in isopropanol (200 mL) was added 1-chlorobutane (221 mL, 2.05 mol). The mixture was heated with stirring to 40 °C for 72 hours. The solution was then allowed to cool to -14 °C and the isopropanol was decanted from the crystalline solid. The resulting solid was washed with ethyl acetate (3×75 mL) until white crystals were obtained. The solid was then recrystallised from isopropanol (100 mL) and dried *in vacuo* for 24 hours, affording [$\text{C}_4\text{C}_1\text{py}$] Cl as a white crystalline solid (280.1 g, 82.6 %).

δ_{H} : (400 MHz, $\text{DMSO}-d^6$) / ppm 3.69-3.40 (6H, m, $\text{N}(\text{CH}_2)_2$ and $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 3.06 (3H, s, NCH_3), 2.02 (4H, s, $\text{NCH}_2(\text{CH}_2)_2$), 2.08 (4H, s, CH_2 -3,4), 1.63 (2H, m, $J = 7.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.24 (2H, sextet, $^3J = 7.3$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.86 (3H, t, $^3J = 7.3$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

δ_{C} : (100 MHz, $\text{DMSO}-d^6$) / ppm 62.8 (s, NCH_2), 62.1 (s, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 47.0 (s, NCH_3), 24.9 (s, $\text{NCH}_2(\text{CH}_2)_2$), 21.0 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.2 (s, $\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$), 13.40 (s, $\text{N}(\text{CH}_2)_3\text{CH}_3$).

m/z (FAB⁺): 319, $[(C_4C_1py)_2Cl]^+$, 17%) and 142, $[(C_4C_1py)]^+$, 100%)

m/z (FAB⁻): 212, $[(C_4C_1py)Cl_2]^-$, 100%) and 35 (Cl^- , 52 %)

Elemental (calc.): %C = 60.62 (60.83), %H = 11.44 (11.34), %N = 7.92 (7.88).

Synthesis of 1-butyl-2,3-dimethylimidazolium chloride, $[C_4C_1C_1im]Cl$ As for the preparation of $[C_4C_1im]Cl$ except, chlorobutane (65 mL, 0.620 mol) and 1,2-dimethylimidazole (50 mL, 0.564 mol) used to afford $[C_4C_1C_1im]Cl$ (89.1, 83.8 %) as a colourless crystalline solid.

δ_H : (400 MHz, DMSO- d^6) / ppm 7.78 (1H, s, NCH), 7.53 (1H, s, NCH), 4.12 (2H, t, $^3J = 7.3$ Hz, $NCH_2(CH_2)_2CH_3$), 3.73 (3H, s, NCH_3), 2.60 (3H, s, N_2CCH_3), 1.74 (2H, quintet, $^3J = 7.4$ Hz, $NCH_2CH_2CH_2CH_3$), 1.28 (2H, sextet, $^3J = 7.5$ Hz, $NCH_2C_2CH_2CH_3$), and 0.88 (3H, t, $^3J = 7.3$ Hz, $N(CH_2)_3CH_3$).

δ_C : (100 MHz, DMSO- d^6) / ppm 144.4 (s, N_2C), 122.2 and 120.8 (s, 2NCH), 47.4 (s, $NCH_2(CH_2)_2CH_3$), 34.5 (s, NCH_3), 31.2 (s, $NCH_2CH_2CH_2CH_3$), 18.9 (s, $NCH_2C_2CH_2CH_3$), 13.3 (s, $N(CH_2)_3CH_3$) and 8.9 (s, N_2CCH_3).

m/z (FAB⁺): 342 $[(C_4C_1C_1im)_2Cl]^+$, 22%) and 153 $[(C_4C_1C_1im)]^+$, 100%)

m/z (FAB⁻): 188 ($[matrix + Cl]^-$, 100 %)

Elemental Analysis (predicted): %C = 57.28 (57.29), %H = 9.26 (9.08) and %N = 14.72 (14.85)

Synthesis of 1-butyl-1-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_4C_1im][NTf_2]$ In a Schlenk tube, lithium bis(trifluoromethylsulfonyl)imide (144 g, 0.499 mol) was added to a solution of $[C_4C_1im]Cl$ (84.5 g, 0.484 mol) in dichloromethane (200 mL). The resulting suspension was stirred for 48 hours, then filtered. The residual salt was washed with dichloromethane (2 x 30 mL) and the combined organic extracts were washed with water until the aqueous phase was halide free (by silver nitrate test), after which the solvent was removed *in vacuo*. The resulting liquid was treated with activated charcoal and filtered through a pad of acidic alumina to give a colourless liquid (186g, 91.9%).

δ_H : (400 MHz, DMSO- d^6) / ppm 9.06 (1H, s, CH-2), 7.64 (2H, 2 s, CH-4,5), 4.12 (2H, t, N-CH₂-), 3.83 (3H, s, N-CH₃), 1.73 (2H, quintet, N-CH₂-CH₂-), 1.23 (2H, sextet, N-CH₂-CH₂-CH₂-), 0.86 (3H, t, N-CH₂-CH₂-CH₂-CH₃).

δ_C : (100 MHz, DMSO- d^6) / ppm 136.5 (s, N_2C), 126.6 and 122.2 (2 s, 2 NCH), 119.6 (q, $^1J_{13C-19F} = 321.8$ Hz, $[N(SO_2CF_3)_2]^-$), 48.7 (s, $NCH_2(CH_2)_2CH_3$), 35.6 (s, NCH_3), 31.4 (s, $NCH_2CH_2CH_2CH_3$), 18.8 (s, $N(CH_2)_2CH_2CH_3$) and 12.9 (s, $N(CH_2)_3CH_3$).

m/z (FAB⁺): 558 $[(C_4C_1im)_2(NTf_2)]^+$, 45%) and 139 $[(C_4C_1im)]^+$, 100 %)

m/z (FAB⁻): 280 $[(NTf_2)]^-$, 100 %)

Elemental (calc.): %C = 28.65 (28.60), %H = 3.49 (3.61), %N = 9.85 (10.02).

Synthesis of N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[C_4C_1py][NTf_2]$ As for the synthesis of $[C_4C_1im][N(Tf)_2]$ except $[C_4C_1py]Cl$ (31.2 g, 0.18 mol) and lithium bis(trifluoromethylsulfonyl)imide (50.0 g, 0.18 mol) used to afford $[C_4C_1py][N(Tf)_2]$ (65.0 g, 87.7%), a colourless liquid.

δ_{H} : (400 MHz, DMSO- d^6) / ppm 3.45 (4H, m, CH_2 -4,5), 3.30 (2H, t, N- CH_2 -), 2.96 (3H, s, N- CH_3), 2.08 (4H, s, CH_2 -3,4), 1.65 (2H, quintet, N- CH_2 - CH_2 -), 1.30 (2H, sextet, N- CH_2 - CH_2 - CH_2 -), 0.93 (3H, t, N- CH_2 - CH_2 - CH_2 - CH_3).

δ_{C} : (100 MHz, DMSO- d^6) / ppm 119.5 (q, $^1J_{13\text{C}-19\text{F}} = 321.6$ Hz, $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$), 63.5 (s, $\text{N}(\text{CH}_2)_2$), 63.1 (s, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2$), 47.5 (s, NCH_3), 24.9 (s, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 21.0 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.2 (s, $\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$), 13.2 (s, $\text{N}(\text{CH}_2)_3\text{CH}_3$).

m/z (FAB $^+$): 564 ($[(\text{C}_4\text{C}_1\text{py})_2(\text{NTf})]^+$, 31%) and 142 ($[\text{C}_4\text{C}_1\text{py}]^+$, 100%)

m/z (FAB $^-$): 280 ($[\text{NTf}_2]^-$, 100%)

Elemental (calc.): %C = 31.38 (31.28), %H = 4.86 (4.77), %N = 6.51 (6.63).

Synthesis of 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, $[\text{C}_4\text{C}_1\text{C}_1\text{im}][\text{NTf}_2]$

As for the synthesis of $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$ except $[\text{C}_4\text{C}_1\text{C}_1\text{im}]\text{Cl}$ (30.9 g, 0.164 mol) and lithium bis(trifluoromethylsulfonyl)imide (48.8 g, 0.169 mol) used to afford $[\text{C}_4\text{C}_1\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$ (71.0 g, 89.0%), a colourless liquid.

δ_{H} : (400 MHz, DMSO- d^6) / ppm 7.58 (2H, AB quartet, $^3J_{\text{A-B}} = 1.97$ Hz, 2NCH), 4.12 (2H, t, $^3J = 7.3$ Hz, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 3.77 (3H, s, NCH_3), 2.59 (3H, s, N_2CCH_3), 1.73 (2H, quintet, $^3J = 7.5$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.32 (2H, sextet, $^3J = 7.5$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), and 0.92 (3H, t, $^3J = 7.3$ Hz, $\text{N}(\text{CH}_2)_3\text{CH}_3$).

δ_{C} : (100 MHz, DMSO- d^6) / ppm 144.2 (s, N_2C), 122.26 and 120.8 (s, 2NCH), 119.8 (q, $^1J_{13\text{C}-19\text{F}} = 321.6$ Hz, $[\text{N}(\text{SO}_2\text{CF}_3)]^-$), 47.4 (s, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 34.5 (s, NCH_3), 31.2 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.9 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.1 (s, $\text{N}(\text{CH}_2)_3\text{CH}_3$) and 8.92 (s, N_2CCH_3).

m/z (FAB $^+$): 586 ($[(\text{C}_4\text{C}_1\text{C}_1\text{im})_2(\text{NTf}_2)]^+$, 20%) and 153 ($[\text{C}_4\text{C}_1\text{C}_1\text{im}]^+$, 100%)

m/z (FAB $^-$): 280 ($[\text{N}(\text{Tf})_2]^-$, 100 %)

Elemental Analysis (predicted): %C = 30.52 (30.69), %H = 4.00 (3.95) and %N = 9.51 (9.70)

Synthesis of 1-butyl-1-methylimidazolium trifluoromethanesulfonate, $[\text{C}_4\text{C}_1\text{im}][\text{OTf}]$ In a Schlenk tube, lithium triflate (33.5g, 0.329 mol) was added to a solution of $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ (55.7 g, 0.319 mol) in dichloromethane (200 mL). The resulting suspension was stirred for 48 hours and then filtered. The residual salt was washed with dichloromethane (2 x 30 mL) and the combined organic extracts were washed with water until the aqueous phase was halide free (by silver nitrate test), after which the solvent was removed *in vacuo*. The resulting liquid was treated with activated charcoal and filtered through a pad of acidic alumina to give a colourless liquid (74.7 g, 61.2 %).

δ_{H} : (400 MHz, DMSO- d^6) / ppm 9.09 (1H, s, CH-2), 7.76 (1H, s, CH-5), 7.68 (1H, s, CH-4), 4.16 (2H, t, N- CH_2 -), 3.84 (3H, s, N- CH_3), 1.76 (2H, quintet, N- CH_2 - CH_2 -), 1.25 (2H, sextet, N- CH_2 - CH_2 - CH_2 -), 0.90 (3H, t, N- CH_2 - CH_2 - CH_2 - CH_3).

δ_{C} : (100 MHz, DMSO- d^6) / ppm 136.4 (s, N_2C), 123.5 and 122.2 (2 s, 2 NCH), 120.7 (q, $^1J_{13\text{C}-19\text{F}} = 321.6$ Hz, $[\text{OSO}_2\text{CF}_3]^-$), 48.4 (s, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 35.6 (s, NCH_3), 31.3 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.7 (s, $\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$) and 13.1 (s, $\text{N}(\text{CH}_2)_3\text{CH}_3$).

m/z (FAB $^+$) MS: 373 ($[(\text{C}_4\text{C}_1\text{im})_2(\text{OTf})]^+$, 13.0 %) and 139 ($[\text{C}_4\text{C}_1\text{im}]^+$, 100 %)

m/z (FAB $^-$) MS: 437, ($[(\text{C}_4\text{C}_1\text{im})(\text{OTf})_2]^-$, 3.12 %) and 149 ($[\text{OTf}]^-$, 100 %)

Elemental (calc.): %C = 37.33 (37.50), %H = 5.22 (5.24), %N = 9.54 (9.72).

Figure A: Integrated Rate Equation (IRE) against time for Brönsted acid catalysed esterification in toluene.

Figure B: IRE against time for Brönsted acid catalysed esterification in acetonitrile.

Figure C: IRE against time for Brønsted acid catalysed esterification in $[C_4C_{1im}][N(Tf)_2]$.

Figure D: IRE against time for Brønsted acid catalysed esterification in $[C_4C_{1im}][OTf]$.

Figure E: IRE against time for Brønsted acid catalysed esterification in $[C_4C_1C_1im][N(Tf)_2]$.

Figure F: IRE against time for Brønsted acid catalysed esterification in $[C_4C_1py][N(Tf)_2]$.

Figure G: IRE against time for Brönsted acid catalysed esterification in THF.

Derivation of second order rate law by integration

$$\frac{d[P]}{dt} = k_2[\text{alcohol}][\text{acid}]$$

$$\int_0^x \frac{d[\text{ester}]}{[\text{alcohol}][\text{acid}]} = \int_0^t k_2 dt$$

Define $x = \frac{[\text{ester}]}{[\text{alcohol}]_0}$

Therefore $[\text{ester}] = x[\text{alcohol}]_0$

Define $\theta_{\text{acid}} = \frac{[\text{acid}]_0}{[\text{alcohol}]_0}$

Therefore $[\text{acid}]_0 = [\text{alcohol}]_0 \times \theta_{\text{acid}}$

So if $[\text{alcohol}] = [\text{alcohol}]_0 - [\text{ester}]$

Then $[\text{alcohol}] = [\text{alcohol}]_0 - x[\text{alcohol}]_0$

And $[\text{acid}] = [\text{alcohol}]_0 \times \theta_{\text{acid}} - x[\text{alcohol}]_0$

Therefore $\int_0^x \frac{[\text{alcohol}]_0 dx}{([\text{alcohol}]_0 - x[\text{alcohol}]_0)([\text{alcohol}]_0 \times \theta_{\text{acid}} - x[\text{alcohol}]_0)} = \int_0^t k_2 dt$

And $\int_0^x \frac{[\text{alcohol}]_0 dx}{[\text{alcohol}]_0^2 (1-x)(\theta_{\text{acid}} - x)} = \int_0^t k_2 dt$

And $\frac{1}{[\text{alcohol}]_0} \int_0^x \frac{dx}{(1-x)(\theta_{\text{acid}} - x)} = \int_0^t k_2 dt$

And $\frac{1}{[\text{alcohol}]_0} \int_0^x \frac{dx}{(1-x)(\theta_{\text{acid}} - x)} = k_2 t$

And (via partial fraction integration)

$$\frac{1}{[\text{alcohol}]_0} \times \frac{1}{\theta_{\text{acid}} - 1} \times \ln \frac{(\theta_{\text{acid}} - x)}{\theta_{\text{acid}}(1-x)} = k_2 t$$

To check derivation:

Moore, J. W., Pearson, R. G., *Kinetics and Mechanism*, 3rd Ed., John Wiley and Sons, 1981 defines the integrated second order rate law when reagents are not in equimolar amounts as:

$$k_2 t = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}$$

Where:

$$x = \frac{\xi}{V}$$

a = initial concentration of reactant a

b = initial concentration of reactant b

V = volume of reaction

ξ = moles of product formed

In our study we define:

reactant a = alcohol

reactant b = acid

Therefore:

$$a = [\text{alcohol}]_0$$

$$b = [\text{acid}]_0$$

Furthermore we define:

$$\theta_{\text{acid}} = \frac{[\text{acid}]_0}{[\text{alcohol}]_0}$$

$$x = \frac{[\text{ester}]}{[\text{alcohol}]_0}$$

$$x = \frac{\xi}{V} = [\text{ester}]$$

Therefore:

$$x = x' [\text{alcohol}]_0$$

In this expression we have uses the parenthesis to differentiate between moles of product (x) and conversion (x'). For neatness, in the paper we simply define the conversion as x in equation 3 (the more-standard definition of x).

As such:

$$b = [\text{acid}]_0 = \theta_{\text{acid}} [\text{alcohol}]_0$$

Substituting into the integrated second order rate law yields:

$$k_2 t = \frac{1}{\theta_{\text{acid}} [\text{alcohol}]_0 - [\text{alcohol}]_0} \ln \frac{[\text{alcohol}]_0 (\theta_{\text{acid}} [\text{alcohol}]_0 - x' [\text{alcohol}]_0)}{\theta_{\text{acid}} [\text{alcohol}]_0 ([\text{alcohol}]_0 - x' [\text{alcohol}]_0)}$$

Factor out $[\text{alcohol}]_0$ where possible:

$$k_2 t = \frac{1}{[\text{alcohol}]_0 (\theta_{\text{acid}} - 1)} \ln \frac{[\text{alcohol}]_0^2 (\theta_{\text{acid}} - x')}{\theta_{\text{acid}} [\text{alcohol}]_0^2 (1 - x')}$$

Cancel $[\text{alcohol}]_0$ where possible and split first term:

$$k_2 t = \frac{1}{[\text{alcohol}]_0 (\theta_{\text{acid}} - 1)} \ln \frac{(\theta_{\text{acid}} - x')}{\theta_{\text{acid}} (1 - x')}$$

Calculations:

$[\text{alcohol}]_0$ is calculated from starting mass of alcohol and volume of reaction and is always approximately 1 mol dm^{-3} .

x' and θ_{acid} are unitless ratios. As such, they do not have to be calculated from concentrations and can

instead be calculated directly from ^1H NMR integrals according to the following formulae:

$$x' = \frac{I_{a'}}{I_{a'} + I_a}$$

$$\theta_{\text{acid}} = \frac{I_{b'} + I_b}{I_{a'} + I_a}$$

Where the integrals ($I_{\text{subscript}}$) correspond to resonances for the following protons: