Electronic Supporting Information

The Amphiphilic Nanostructure of Ionic Liquids Affects the Dehydration of Alcohols

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General experimental considerations

The alcohol reagents purchased were of the highest purity available and dried using appropriate drying agents. Reagents used in the synthesis of ILs were purified immediately prior to their use. 1-methylimidazole was dried over potassium hydroxide and distilled under a nitrogen atmosphere. Bromoethane, 1-bromobutane, 1-chlorohexane, 1-chlorooctane, 1-bromodecane and 1-chlorodecane were distilled under nitrogen (bromoethane and 1-bromobutane) or under reduced pressure (1-chlorohexane, 1-chlorooctane, 1-bromodecane and 1-chlorodecane). [$C_4C_1C_1^2$im], [C_6C_1im], [C_8C_1im] and [$C_{10}C_1$im] based ILs were synthesized according to the methods outlined for analogous [C_4C_1im] containing ILs in literature.[1] NMR spectra were recorded on a Bruker DRX-400 spectrometer.

Synthesis of ionic liquids

Synthesis of 1-ethyl-3-methylimidazolium bromide

Using the method of Brooks et al,[1] distilled bromoethane (64.45 g, 0.592 mol) and 1-methylimidazole (44.37 g, 0.540 mol) were mixed with ethyl acetate (100 mL), the resultant solution was stirred at 40°C for 24 h. Upon cooling to room temperature, a white solid formed. After decanting off the ethyl acetate, the solid was dried in vacuo at 50 °C for 24 h. The 1-ethyl-3-methylimidazolium bromide formed was recrystallized from a solution of acetonitrile and ethyl acetate to remove unreacted 1-methylimidazole, then dried again in vacuo to yield [C_2C_1im]Br as a white solid (86.89 g, 0.455 mol, 84.2%).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d_6): 9.18 (s, 1H), 7.81 (t, J = 1.8 Hz, 1H), 7.72 (t, J = 1.8 Hz, 1H), 4.21 (q, J = 7.3 Hz, 2H), 3.87 (s, 3H), 1.43 (t, J = 7.3 Hz, 3H)

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d_6): 136.25, 123.53, 121.96, 44.10, 35.71, 15.14

Synthesis of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

Using the methods of Brooks et al,[1] 1-ethyl-3-methylimidazolium bromide (44.71 g, 0.234 mol) and lithium bis(trifluoromethylsulfonyl)imide (75.36 g, 0.263 mol) were separately dissolved in deionized water (150 mL for both). These aqueous solutions were combined resulting in the immediate formation of a second phase. Dichloromethane (150 mL) was added to increase the volume of the lower phase and the resultant organic phase was separated and washed with water until the aqueous phase tested negative for halide using 0.1 M silver nitrate solution (6 x 150 mL). The dichloromethane was removed and the resultant liquid dried at 50ºC in vacuo to yield $[C_2C_1im][NTf_2]$ as a colourless liquid (81.64 g, 0.209 mol, 89.2%).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d6): 9.11 (s, 1H), 7.77 (t, J = 1.8 Hz, 1H), 7.69(t, J = 1.8 Hz, 1H), 4.20 (q, J = 7.3 Hz, 2H), 3.86 (s, 3H), 1.43 (t, J = 7.3 Hz, 3H)

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d6): 136.21, 123.53, 121.92, 44.11, 35.62, 14.98.

^{19}F NMR δ (ppm) (400 MHz, DMSO-d6): -78.74 (s)

Synthesis of 1-butyl-3-methylimidazolium bromide

Using the method of Brooks et al,[1] distilled 1-bromobutane (127.2 g, 0.928 mol) and 1-methylimidazole (61.8 g, 0.754 mol) were mixed with ethyl acetate (100 mL), and the resultant solution was stirred at 40 °C for 24 h. Upon cooling to room temperature, a white solid formed. After decanting off the ethyl acetate, the solid was dried in vacuo at 50 °C for 24 h. The 1-butyl-3-methylimidazolium bromide formed was recrystallized from a solution of acetonitrile and ethyl acetate to remove unreacted 1-methylimidazole, then dried again in vacuo to yield $[C_4C_1im]Br$ as a white solid (151.2 g, 91.5 % yield).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d_6): 9.31 (m, 1H), 7.8 (m, 2H), 4.19 (t, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.43 – 3.25 (m, 1H), 1.90 – 1.59 (m, 2H), 1.25 (td, J = 7.4, 2.4 Hz, 2H), 0.88 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d_6): 136.48, 123.49, 122.20, 48.38, 35.72, 31.30 , 18.68, 13.21.

Synthesis of silver dicyanamide

Silver nitrate (13.122 g, 77 mmol) was dissolved in deionised water (~100 mL). Sodium dicyanamide (6.878 g, 77 mmol) was added to the aqueous silver nitrate solution and the solution stirred for 1 h in the dark. The solid was isolated by filtration and washed with deionised water. The white solid was dried at the pump for 2 h then further dried in vacuo at 55°C for 16 h to yield $AgN(CN)_2$ as a white

solid (12.45 g, 0.0716 mol, 92.67 %).

IR (cm-1) – 3598.82, 3081.95, 2302.78, 2248.78, 2175.49 v($C \equiv N$), 1361.61 v($C - N$), 952.74, 648.02, 489.87.

Synthesis of 1-butyl-3-methylimidazolium dicyanamide

1-butyl-3-methylimidazolium bromide (22.69 g, 0.104 mol) was dissolved in deionized water (150 mL). Silver dicyanamide (18.0 g, 0.1035 mol) was added to this solution and stirred in the dark for 16 h. The resultant slurry was then filtered and the solution checked for the removal of bromide by testing with saturated aqueous $AgN(CN)_2$ solution (0.1 g of $AgN(CN)_2$ in 50 mL of water). More $AgN(CN)_2$ was added until no more AgBr precipitate was observed using the $Ag[N(CN)_2]$ test. After the final filtration, water was removed using a rotary evaporator and then dichloromethane (~200 mL) was added to precipitate any remaining dissolved salts. The solution was filtered, solvent removed by rotary evaporation and the resultant colourless liquid dried in vacuo at 50 °C for 16 h to yield $[C_4C_1im][N(CN)_2]$ as a colourless moderately viscous liquid (15.79 g, 0.0769 mol, 74.29%).

^{1}H NMR δ (ppm) (400 MHz, DMSO) 9.15 (s, 1H), 7.77 (t, J = 1.7 Hz, 1H), 7.70 (t, J = 1.6 Hz, 1H), 4.21 (t, J = 7.2 Hz, 2H), 3.90 (s, 3H), 1.81 (quint, J = 12.8, 7.5 Hz, 2H), 1.39 (sext, 2H), 0.92 (t, J = 7.4 Hz, 3H).

^{13}C NMR δ (ppm) (400 MHz, DMSO) 136.49, 123.49, 122.16, 119.06, 48.56, 35.66, 31.32, 18.76, 13.12.

HRMS found (ESI): m/z 139.1229 (100%, $[C_4C_1im]^+$), 66.0096 (100%, $[N(CN)_2]^-$)

Synthesis of 1-butyl-3-methylimidazolium trifluoromethanesulfonate

Using the method of Brooks et al,[1] 1-butyl-3-methylimidazolium bromide (98.9 g, 0.452 mol) was dissolved in dichloromethane and added to a stirred slurry of sodium trifluoromethanesulfonate (83.5 g, 0.485 mol) in dichloromethane, and the resultant slurry stirred at room temperature for 48 h. The solution was vacuum filtered to remove solid sodium bromide. The dichloromethane solution was then successively washed with water until all bromide was removed, determined by testing with a 0.1 M silver nitrate solution. Excess dichloromethane was removed by rotary evaporator, and the $[C_4C_1im][OTf]$ formed was dried under high vacuum at 50 °C for 24 h to afford a colourless liquid (123.6 g, 94.9%).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d_6): 9.10 (m, 1H), 7.74 (dt, J = 26.9, 1.8 Hz, 2H), 4.17 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.84 – 1.71 (m, 2H), 1.35 – 1.20 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR δ (ppm) (400 MHz, DMSO-d_6): 136.47, 123.59, 122.24, 48.48, 35.71, 31.31, 18.73, 13.21.

^{19}F NMR δ (ppm) (400 MHz, DMSO-d_6): -77.76 (s, CF_3)

Synthesis of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

1-Butyl-3-methylimidazolium bromide (62.28 g, 0.284 mol) and lithium bis(trifluoromethanesulfonyl)imide (81.27 g, 0.300 mol) were separately dissolved in water (100 mL). These solutions were combined and stirred, leading to the formation of a biphasic mixture. Dichloromethane (150 mL) was added to increase the volume of the lower phase and the resultant organic phase separated using a separatory funnel. The organic phase was washed with deionized water (~ 150 mL) 3-4 times until all bromide was removed, determined by testing the water layer after washing with 0.1 M $AgNO_3$ solution. Dichloromethane was removed by rotary evaporation and the resultant liquid dried in *vacuo* at 50 °C for 16 h to afford $[C_4C_1im][NTf_2]$ as a clear colourless oil (109.82 g, 0.261 mol, 91.8%).

^1H NMR δ (ppm) (400 MHz, DMSO) 9.11 (s, 1H), 7.73 (t, J = 1.8 Hz, 1H), 7.67 (t, J = 1.7 Hz, 1H), 4.18 (t, J = 7.2 Hz, 2H), 3.88 (s, 3H), 1.80 (quint, J = 7.5 Hz, 2H), 1.53 – 1.18 (sext, 2H), 0.92 (t, J = 7.4 Hz, 3H)
$^{13}C\{^1H\}$ NMR δ (ppm) (101 MHz, DMSO) 136.93 (s), 124.75 (s), 123.96 (s), 122.61 (q, J =321.7 Hz), 49.03 (s), 36.01 (s), 31.76 (s), 19.13 (s), 13.36 (s).
^{19}F NMR δ (ppm) (376 MHz, DMSO) -77.17 (s)
HRMS found (ESI): m/z 139.1228 (100%, $[C_4C_1im^+]$), 279.9182 (100 %, $[NTf_2]^-$)

Synthesis of 1-butyl-2,3-dimethylimidazolium bromide

Distilled 1-bromobutane (63.5 g, 0.463 mol) and 1,2-dimethylimidazole (39.9 g, 0.415 mol) were dissolved in ethyl acetate (150 ml), and the resultant solution was stirred at 50 °C for 48 h, leading to formation of a white crystalline solid. After decanting off the ethyl acetate, the solid was dried in vacuo at 50 °C for 24 h. The 1-butyl-2,3-dimethylimidazolium bromide formed was recrystallized from a solution of acetonitrile and ethyl acetate to remove unreacted 1,2-dimethylimidazole, then dried again in vacuo to yield $[C_4C_1C_1{}^2im]Br$ as a white solid (89.8 g, 92.8 % yield).

^1H NMR δ (ppm) (400 MHz, DMSO-d_6): 7.73 (t, J = 7.3 Hz, 1H), 7.70 (t, J = 7.3 Hz, 1H), 4.19 (t, J = 7.3 Hz, 3H), 3.83 (s, 2H), 2.67 (s, 3H), 1.84 – 1.68 (m, 2H), 1.43 – 1.30 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR δ (ppm) (400 MHz, DMSO-d_6): 144.18, 122.27, 120.95, 47.27, 34.60, 31.14, 18.84, 13.29, 9.05.

Synthesis of 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide

1-butyl-2,3-dimethylimidazolium bromide (30.7 g, 0.131 mol) and lithium bis(trifluoromethanesulfonyl)imide (38.5 g, 0.134 mol) were separately dissolved in water (50 mL). The aqueous solutions were mixed together and placed into a separatory funnel. Dichloromethane (150 mL) was added and the organic layer was separated and washed with water until all bromide was removed, determined by testing with a 0.1 M silver nitrate solution. Excess dichloromethane was removed by rotary evaporator, and the 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide formed was dried in vacuo at 50 °C for 24 h to afford $[C_4C_1C_1{}^2im][NTf_2]$ as a colourless liquid (53.4 g, 94 % yield).

^1H NMR δ (ppm) (400 MHz, DMSO-d_6): 7.65 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.3 Hz, 1H), 4.12 (t, J = 7.3 Hz, 3H), 3.76 (s, 2H), 2.59 (s, 3H), 1.78 – 1.63 (m, 2H), 1.39 – 1.20 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR δ (ppm) (400 MHz, DMSO-d_6): 144.18, 122.27, 120.95, 117.88, 47.27, 34.60, 31.14, 18.84, 13.29, 9.05.

^{19}F NMR δ (ppm) (400 MHz, DMSO-d_6): -78.74 (s, CF_3)

Synthesis of 1-hexyl-3-methylimidazolium chloride

Distilled 1-chlorohexane (60.37 g, 0.505 mol) and 1-methylimidazole (43.48 g, 0.529 mol) were dissolved in ethyl acetate (150 mL), and the resultant solution was stirred at 70ºC for 24 days. After decanting off the ethyl acetate, the ionic liquid was dried in vacuo at 55ºC for 24 h. The 1-hexyl-3-methylimidazolium chloride formed was washed with diethyl ether to remove unreacted 1-methylimidazole, then dried again in vacuo to yield $[C_6C_1im][Cl]$ as a pale-yellow liquid (87.1 g, 0.429 mol, 81.1 %).

^1H NMR δ (ppm) (400 MHz, DMSO-d_6): 9.43 (s, 1H), 7.85 (t, J = 1.8 Hz, 1H), 7.78 (t, J = 1.7 Hz, 1H), 4.19 (t, J = 7.2 Hz, 2H), 3.88 (s, 3H), 1.85 – 1.70 (m, 8H), 0.91 – 0.79 (m, 3H).

$^{13}C\{^1H\}$ NMR δ (ppm) (400 MHz, DMSO-d_6): 136.49, 123.59, 122.25, 48.73, 35.75, 30.52, 29.32, 25.12, 21.85, 13.82

Synthesis of 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

1-hexyl-3-methylimidazolium chloride (15.13 g, 0.0746 mol) and lithium bis(trifluoromethylsulfonyl)imide (17.66 g, 0.0784 mol) were dissolved separately in water (100 mL) then combined. Dichloromethane (150 mL) was added to extract the ionic liquid. The dichloromethane layer was separated, then washed with deionized water (4×100 mL) until all chloride was removed, determined by testing with a 0.1 M silver nitrate solution. Dichloromethane was removed by rotary evaporator and the resultant liquid dried in vacuo at 55°C to yield $[C_6C_1im]$ $[NTf_2]$ as a clear colorless liquid (25.4 g, 0.0506 mol, 76.2%).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d6): 9.11 (s, 1H), 7.77 (t, J = 1.8 Hz, 1H), 7.70 (t, J = 1.7 Hz, 1H), 4.16 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.85 – 1.73 (m, 2H), 1.36 – 1.19 (m, 8H), 0.94 – 0.84 (m, 3H).

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d6): 136.47, 123.60, 122.24, 119.47, 48.76, 35.71, 30.51, 29.30, 25.11, 21.83, 13.77.

^{19}F NMR δ (ppm) (400 MHz, DMSO-d6): -78.72.

Synthesis of 1-octyl-3-methylimidazolium chloride

Distilled 1-chlorooctane (86.35 g, 0.581 mol) and 1-methylimidazole (50.01 g, 0.6091 mol) were dissolved in ethyl acetate (160 mL), and the resultant solution stirred at 80ºC for 35 days. After decanting off the ethyl acetate the ionic liquid was dried in vacuo at 60ºC for 24 h. The 1-octyl-3-methylimidazolium chloride formed was washed with diethyl ether to remove unreacted 1-methylimidazole, then dried again in vacuo to yield $[C_8C_1im]Cl$ as a colourless liquid (100.74 g, 0.437 mol, 71.66 %).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d6): 10.23 (s, 1H), 9.27 (s, 1H), 7.81 (t, J = 1.8 Hz, 1H), 7.74 (t, J = 1.7 Hz, 1H), 4.18 (t, J = 7.2 Hz, 2H), 3.87 (s, 3H), 1.85 – 1.72 (m, 2H), 1.34 – 1.19 (m, 10H), 0.90 – 0.83 (m, 3H).

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d6): 136.60, 123.58, 122.25, 48.72, 35.71, 31.14, 29.38, 28.39, 25.48, 22.03, 13.92.

Synthesis of 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

1-octyl-3-methylimidazolium chloride (15.14 g, 0.066 mol) and lithium bis(trifluoromethylsulfonyl)imide (19.78 g, 0.069 mol) were dissolved separately in water (100 mL), then combined. Dichloromethane (150 mL) was added to extract the ionic liquid. The dichloromethane layer was separated, then washed with deionised water (4×100 mL) until all bromide was removed,

determined by testing with a 0.1 M silver nitrate solution. Dichloromethane was removed by rotary evaporator and the resultant liquid dried in vacuo at 55℃ to yield [C_8C_1im] [NTf_2] as a clear colorless liquid (29.9 g, 0.0629 mol, 95.83%).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d6): 9.11 (s, 1H), 7.77 (t, J = 1.8 Hz, 1H), 7.70 (t, J = 1.7 Hz, 1H), 4.16 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.85 – 1.73 (m, 2H), 1.29 (m, 12H), 0.92 – 0.83 (t, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d6): 136.47, 123.60, 122.25, 119.48, 48.77, 35.72, 31.13, 29.35, 28.44, 28.30, 25.46, 22.02, 13.89.

^{19}F NMR δ (ppm) (400 MHz, DMSO-d_6): -78.71.

Synthesis of 1-decyl-3-methylimidazolium bromide

Distilled 1-bromodecane (159.9 g, 0.642 mol) and 1-methylimidazole (51.5 g, 0.627 mol) were dissolved in ethyl acetate (200 mL), and the resultant solution was stirred at 50 °C for 72 h. After decanting off the ethyl acetate, the ionic liquid was dried in vacuo at 50°C for 24 h. The 1-decyl-3-methylimidazolium bromide formed was washed with diethyl ether to remove unreacted 1-methylimidazole, then dried again in vacuo to yield [$C_{10}C_1$im]Br as a colourless liquid (171.4 g, 90.1 %).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d_6): 9.18 (s, 1H), 7.83 (t, J = 1.6 Hz, 1H), 7.76 (t, J = 1.6 Hz, 1H) 4.10 – 3.97 (m, 3H), 3.87 (s, 2H), 1.85 – 1.73 (m, 2H), 1.22 – 1.14 (m, 14H), 0.92 – 0.79 (t, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d6) 136.89, 123.93, 122.63, 49.09, 36.14, 31.64, 29.78, 29.26, 29.19, 29.03, 28.75, 25.85, 22.45, 14.30.

Synthesis of 1-decyl-3-methylimidazolium chloride

Distilled 1-chlorodecane (58.1 g, 0.328 mol) and 1-methylimidazole (25.74 g, 0.312 mol) were dissolved in ethyl acetate (100 mL), and the resultant solution was stirred at 80ºC for 40 days. After decanting off the ethyl acetate, the ionic liquid was dried in vacuo at 50°C for 24 h. The 1-decyl-3-methylimidazolium chloride formed was washed with diethyl ether to remove unreacted 1-methylimidazole, then dried again in vacuo to yield [$C_{10}C_1$im]Cl as a pale-yellow liquid (62.6 g, 0.242 mol, 77.14 %).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d6): 9.09 (s, 1H), 7.75 (t, J = 1.8 Hz, 1H), 7.69 (t, J = 1.7 Hz, 1H), 4.15 (t, J = 7.2 Hz, 2H), 3.85 (s, 3H), 1.83 – 1.72 (m, 2H), 1.25 (s, 14H), 0.86 (t, J = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d6): 136.94, 124.06, 122.71, 121.56, 118.36, 49.26, 36.18, 31.73, 29.83, 29.34, 29.26, 29.11, 28.81, 25.94, 22.53, 14.35.

Synthesis of 1-decyl-3-methylimidazolium dimethylphosphate

1-decyl-3-methylimidazolium chloride (23.66 g, 0.0914 mol) and trimethyl phosphate (31.38 g, 0.224 mol) were mixed with acetonitrile (100 mL), and the resultant solution was stirred at 80ºC for 10 days. The absence of chloride was determined by testing with a 0.1 M silver nitrate solution. Excess acetonitrile was removed by rotary evaporator and the resultant liquid washed with *n*-hexane (100 mL x 30), then dried in vacuo to yield [$C_{10}C_1$im][Me_2PO_4] as a pale-yellow liquid (17.11 g, 0.0491 mol, 53.72 %)

^{1}H NMR δ (ppm) (400 MHz, DMSO-d6): 9.35 (s, 1H), 7.80 (t, J = 1.7 Hz, 1H), 7.73 (t, J = 1.7 Hz, 1H), 4.16 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.83 – 1.72 (m, 2H), 1.24 (m, 14H), 0.86 (t, J = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d6): 136.89, 123.58, 122.26, 51.25, 48.70, 35.65, 31.26, 29.40, 28.88, 28.81, 28.64, 28.37, 25.49, 22.07, 13.92.

^{31}P NMR δ (ppm) (400 MHz, DMSO-d6): 1.10 (sep, J = 10.2 Hz).

Synthesis of 1-decyl-3-methylimidazolium trifluoromethanesulfonate

1-decyl-3-methylimidazolium bromide (100.7 g, 0.304 mol) was dissolved in dichloromethane and added to a stirred slurry of sodium trifluoromethanesulfonate (65.6 g, 0.381 mol) in dichloromethane, and the resultant slurry was stirred at room temperature for 72 h. The solution was vacuum filtered to remove solid sodium bromide. The dichloromethane solution was then successively washed with water until all bromide was removed, determined by testing with a 0.1 M silver nitrate solution. Excess dichloromethane was removed by rotary evaporator, and the [$C_{10}C_1$im][OTf] formed was dried in vacuo at 50 °C for 24 h to yield a colourless liquid (104.7 g, 92.5 %).

^{1}H NMR δ (ppm) (400 MHz, DMSO-d_6): 9.10 (s, 1H), 7.77 (t, J = 1.8 Hz, 1H), 7.71 (t, J = 1.7 Hz, 1H), 4.16 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.79 (m, 2H), 1.41 – 1.12 (m, 14H), 0.87 (t, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR δ (ppm) (400 MHz, DMSO-d_6): 136.46, 123.59, 122.25, 48.76, 35.72, 31.25, 29.34, 28.87, 28.79, 28.63, 28.34, 25.46, 22.06, 13.92

^{19}F NMR δ (ppm) (400 MHz, DMSO-d_6): -78.72 (s, CF_3)

Synthesis of 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

1-Decyl-3-methylimidazolium bromide (15.0 g, 0.0494 mol) and lithium bis(trifluoromethylsulfonyl)imide (14.93 g, 0.0520 mol) were dissolved separately in water (100 mL), then combined. Dichloromethane (150 mL) was added to extract the ionic liquid. The dichloromethane layer was separated, then washed with deionised water (4×100 mL) until all bromide was removed, determined by testing with a 0.1 M silver nitrate solution. Dichloromethane was removed by rotary evaporator and the resultant liquid dried in vacuo at 60°C to yield $[C_{10}C_1im][NTf_2]$ as a clear colorless liquid (23.7 g, 0.0471 mol, 95.2%).

^{1}H NMR δ(ppm) (400 MHz, DMSO-d_6): 9.09 (s, 1H), 7.76 (t, J = 1.8 Hz, 1H), 7.69 (t, J = 1.8 Hz, 1H), 4.14 (t, J = 7.2 Hz, 2H), 3.84 (s, 3H), 1.85 – 1.70 (m, 2H), 1.33 – 1.16 (m, 14H), 0.90 – 0.81 (m, 3H).

^{13}C{^{1}H} NMR δ(ppm) (400 MHz, DMSO-d_6): 136.47, 123.59, 122.24, 121.08, 119.47, 48.76, 35.71, 31.25, 29.35, 28.86, 28.78, 28.63, 28.33, 25.46, 22.06, 13.90.

^{19}F NMR δ(ppm) (400 MHz, DMSO-d_6): -78.72 (s).

Dehydration Reactions

General procedure for cyclohexanol dehydration reaction

Cyclohexanol (250 mg for a typical reaction), mesitylene (internal standard, 20 wt% relative to cyclohexanol, 50 mg for a typical reaction), and IL (1 g for a typical reaction) were combined in a Teflon-lined hydrothermal autoclave and stirred in an oil bath that had been pre-heated to the desired temperature (120-180°C) for the stated reaction time. The reaction was quenched by placing the reactor in an ice bath for 1 h. The reaction mixture was then extracted by hexane (10 × 5 mL) with the combined hexane extracts analysed by GC-FID.

General procedure for kinetic studies of decahydro-2-naphthol dehydration

Decahydro-2-naphthol (100 mg, 6.5×10^{-4} mol) and 1,3,5-trimethoxybenzene (20 mg, 1.19×10^{-4} mol) were added to a solution of IL (1 mL) containing 20 mol% p-toluenesulfonic acid monohydrate (24.6 mg, 1.3×10^{-4} mol) in a sealed 4 mL glass vial. Mixtures were stirred at the desired temperature (100-120 °C) and aliquots were taken at regular intervals, immediately diluted with DMSO-d_6 then analyzed by ^{1}H NMR. The dehydration of decahydro-2-naphthol was carried out at each temperature in $[C_4C_1im][NTf_2]$, $[C_{10}C_1im][NTf_2]$, $[C_4C_1im][OTf]$ and $[C_{10}C_1im][OTf]$. Plots of the time-dependent concentration data collected at different temperatures were then generated.

Procedure for Gas Chromatography with Flame Ionization Detector (GC-FID)

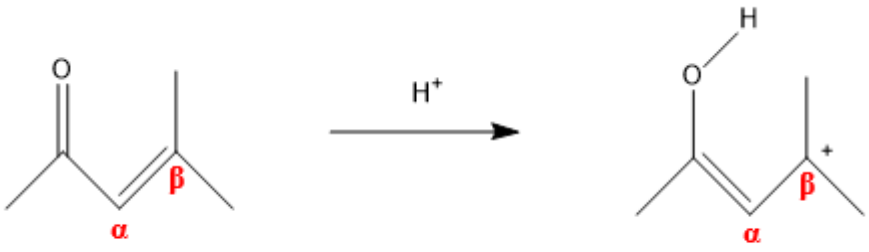
Gas chromatography analysis was performed on a Shimadzu GC-FID 2010 Plus equipped with a DB-FATWAX UI column and flame ionization detector. The analysis of cyclohexanol reaction mixtures was performed using a 29 minute programme with a 1 µL injector volume, split ratio of 40 and injector temperature of 250°C. The oven temperature was initially held at 50 °C for 8 mins, heated at a rate of 10°C min^{-1} then held at 230°C for a further 3 minutes.

Procedure for measuring acidity of ionic liquids

The acidity of p-toluenesulfonic acid in ILs was determined using a literature method for measuring acidity with an NMR probe.[2] Mesityl oxide (2 wt%) was added to a solution of IL (1 mL) containing p-toluenesulfonic acid (24.6 mg, 1.3×10^{-4} mol) in a sealed 4 mL glass vial, and stirred at 50 °C until all solutes were dissolved in the IL. The solution was examined by ^{13}C NMR using a DMSO-d_6 capillary, and the difference in chemical shift (Δδ) between the α and β carbon signals of mesityl oxide shown in Figure S1, was determined. This process was repeated for solutions containing 4 wt% and 6 wt% mesityl oxide. The true acidity of each IL system was extrapolated from the NMR data gathered for each concentration of mesityl oxide.

The Hammett acidity of each IL system was determined using the Hammett acidity equation fitted with the limits of the ^{13}C NMR shifts of mesityl oxide and a slope change.

$$H_0 = -4 - 2.32 \times \log\left(\frac{[\Delta\delta - 31.07]}{[80.91 - \Delta\delta]}\right)$$



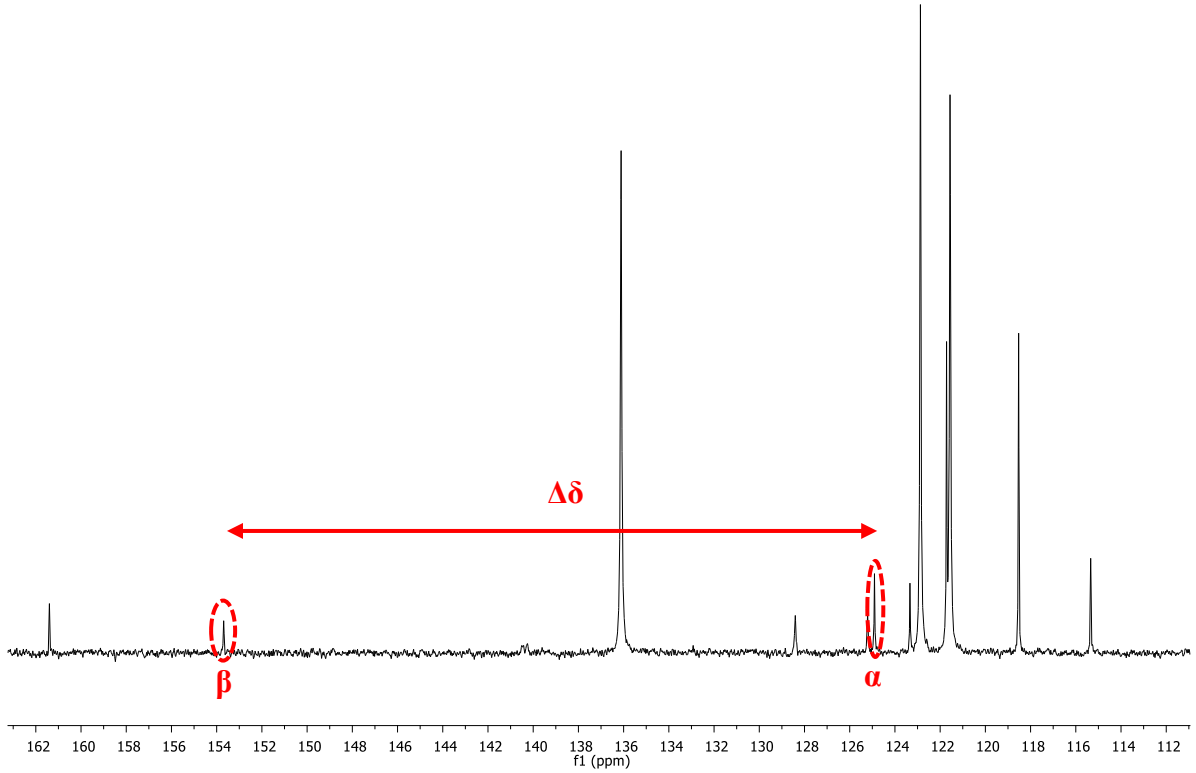


Figure S1. ^{13}C NMR spectrum of [$C_{10}C_1$im][OTf] with p-toluenesulfonic acid and mesityl oxide, reproduced from reference 2. As the acidity of the system increases, so will Δδ between the α and β carbons of mesityl oxide indicated in the reaction scheme.

Further Data and Analysis

Optimisation of reaction conditions for dehydration of cyclohexanol

Table S1: Optimisation of reaction conditions for dehydration of cyclohexanol in [$C_{10}C_1$im][NTf_2] using mesitylene as an internal standard. Standard errors are the standard deviations of replicate reactions where these were performed.

Temperature (ºC)	Reaction time	Cyclohexanol conversion (%)	Cyclohexene yield (%)
150	2 h	16 ± 6	0.8 ± 1.1
150	4 h	8	2.1
180	1 h	30	13
180	2 h	38	21
180	3 h	43 ± 8	25 ± 4

While not quantified by GC-FID, a reaction at 120°C did not yield any discernible product by ^{1}H NMR, leading to the pursuit of higher temperature conditions for the optimisation (shown in Table S1). These optimisation results indicated that a reaction time of 3 h at 180°C was suitable for monitoring the reaction as incomplete cyclohexanol conversion was observed alongside cyclohexene yields of 25%. This provided scope for being able to identify reactions leading to increased and decreased reaction rates within the limits of detection.

Full data for cyclohexanol dehydration in different ionic liquids under standard conditions

Table S2: Yields of cyclohexene and cyclohexanone observed for the dehydration of cyclohexanol under standard conditions (180°C, 3 h) using mesitylene as an internal standard. Reported errors are standard deviations of replicate experiments.

Ionic Liquid	Cyclohexanol (mol fraction)	Cyclohexanol conversion (%)	Cyclohexene yield (%)	Cyclohexanone yield (%)
$[C_2C_1im][NTf_2]$	0.45	59 ± 5	38.7 ± 0.1	2.1 ± 0.1
$[C_4C_1im][NTf_2]$	0.48	58 ± 1	38.7 ± 0.1	1.9 ± 0.1
$[C_6C_1im][NTf_2]$	0.47	52 ± 1	37.3 ± 0.1	1.7 ± 0.1
$[C_8C_1im][NTf_2]$	0.50	38 ± 2	26.1 ± 0.1	1.8 ± 0.1
$[C_{10}C_1im][NTf_2]$	0.12	98 ± 1	26.1 ± 0.5	1.3 ± 0.1
	0.30	87 ± 3	43.7 ± 1.2	1.6 ± 0.1
	0.51	43 ± 8	25 ± 4	2.5 ± 0.7
	0.68	4.4 ± 0.4	1.0 ± 0.1	1.0 ± 0.1
	0.86	7.6 ± 0.1	0.08 ± 0.01	1.0 ± 0.1
$[C_4C_1im][OTf]$	0.32	0[a]	0.6 ± 0.1	2.4 ± 0.1
	0.32[b]	0[a, b]	2.2 ± 0.3[b]	2.4 ± 0.1[b]
$[C_{10}C_1im][OTf]$	0.42	14 ± 2	5 ± 2	2.0 ± 0.3
	0.42[b]	10 ± 3[b]	13 ± 2[b]	2.7 ± 0.3[b]
$[C_4C_1im][N(CN)_2]$	0.30	0[a]	0.7 ± 0.1	1.8 ± 0.1
$[C_{10}C_1im][Me_2PO_4]$	0.42	42 ± 6	0.3 ± 0.1	1.3 ± 0.3
$[C_4C_1C_1^2im][NTf_2]$	0.37	-[c]	0[c]	-[c]

[a] CyOH recovery of >100% observed. [b] Reaction performed for 18 h. [c] Due to GC-FID unavailability, reactions were qualitatively investigated by ^{1}H NMR for the characteristic 5.6 ppm alkene peak of cyclohexene. No peak could be observed indicating that cyclohexene was below the limit of detection (< 1%).

Evidence for the reaction of $[Me_2PO_4]^-$ with cyclohexanol

In $[C_{10}C_1im][Me_2PO_4]$ (Table S2) a relatively high conversion of cyclohexanol was observed (42%) despite negligible amounts of cyclohexene being formed (0.3%). This was investigated further using ^{31}P NMR to elucidate potential side reactions that may be occurring with the IL anion as no additional products were observed by GC-FID. Figure S2 shows the ^{31}P NMR of the reaction mixture. This contains an additional peak which is not present in the original IL or in the reaction mixture. The emergence of this new peak and its chemical shift suggests it is likely to arise from the phosphorylation of cyclohexanol by the $[Me_2PO_4]^-$ anion under the relatively harsh reaction conditions used. As this was not related to the primary aim of this project, this side reaction was not further investigated.

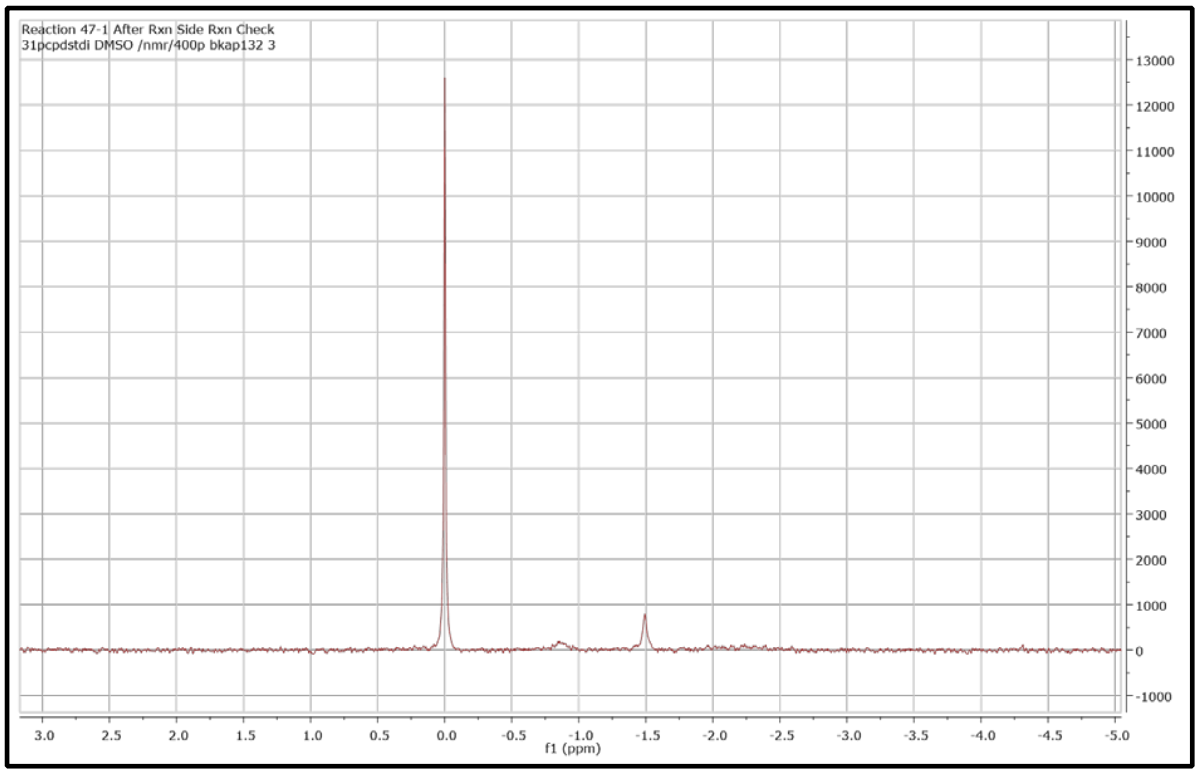


Figure S2: ^{31}P NMR for cyclohexanol dehydration in [$C_{10}C_1$im][Me_2PO_4].

Kinetic plots for dehydration of DHN

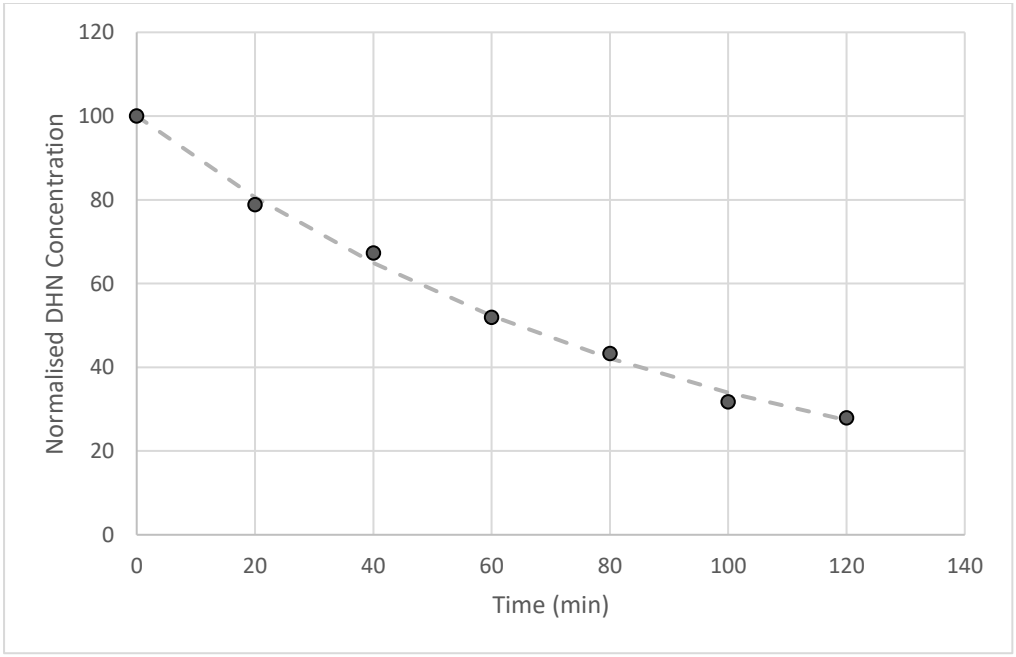


Figure S3. Plot of the relative concentration of decahydro-2-naphthol in [C_4C_1im][OTf] at 120 °C.

Figure S3 shows a representative plot of the concentration of decahydro-2-naphthol over time for a reaction performed at 120 °C in $[C_4C_1im][OTf]$. The data points represent the concentrations of decahydro-2-naphthol obtained from the ratio of the integral of the starting material peak to the internal standard using ^1H NMR. The dashed line represents the concentration fit to a first order rate equation. Note that as these data followed first-order kinetics, normalised concentrations using the internal standard could be used to fit the kinetic model which avoided any error associated with volumetric measurements involving the IL.

Rate constants for dehydration of DHN

The dehydration of decahydro-2-naphthol was monitored using ^1H NMR by following the disappearance of the peak at 3.4 ppm and the appearance of the peaks approximately between 5.5 – 5.65 ppm relative to the 1,3,5-trimethoxybenzene internal standard peak at 6.1 ppm. Tables S3 and S4 summarise the rate constant data and activation parameters calculated from these experiments. Note that the ratio between $[OTf]^-$ rate constants varied with temperature whereas the ratio of the $[NTf_2]^-$ rate constants remained approximately constant. This is an embodiment of the differing activation parameters in these ILs, as demonstrated in Table S4.

Table S3. Rate constants determined for the dehydration of decahydro-2-naphthol in ILs at different temperatures. Errors are standard errors obtained from the linear fits.

Temperature (°C)	$[C_4C_1im][NTf_2]$ (x 10^{-5} s^{-1})	$[C_{10}C_1im][NTf_2]$ (x 10^{-5} s^{-1})	$[C_4C_1im][OTf]$ (x 10^{-5} s^{-1})	$[C_{10}C_1im][OTf]$ (x 10^{-5} s^{-1})
100	2.2 ± 0.04	4.0 ± 0.2	1.4 ± 0.2	0.8 ± 0.06
105	4.5 ± 0.7	8.2 ± 2.4	3.7 ± 0.2	1.4 ± 0.06
110	8.8 ± 0.8	17.6 ± 0.5	5.7 ± 0.02	2.2 ± 0.1
115	16.2 ± 0.5	30.4 ± 2.9	10.9 ± 0.01	4.0 ± 0.06
120	27.4 ± 0.8	54 ± 2.9	17.9 ± 0.1	5.2 ± 0.4

Table S4. Activation and Arrhenius parameters determined for the dehydration of decahydro-2-naphthol in ILs. Errors are standard errors obtained from the linear fits.

Ionic liquid	E_a (kJ mol^{-1})	A (s^{-1})	$\Delta^{\ddagger}H^{O}$ (kJ mol^{-1})	$\Delta^{\ddagger}S^{O}$ (J K^{-1} mol^{-1})
$[C_4C_1im][NTf_2]$	155 ± 4	$1.20 \pm 0.04 \times 10^{17}$	152 ± 4	73 ± 3
$[C_{10}C_1im][NTf_2]$	159 ± 8	$7.3 \pm 0.5 \times 10^{17}$	156 ± 5	88 ± 4
$[C_4C_1im][OTf]$	150 ± 10	$1.8 \pm 0.2 \times 10^{16}$	148 ± 10	57 ± 6
$[C_{10}C_1im][OTf]$	120 ± 7	$4.9 \pm 0.4 \times 10^{11}$	117 ± 7	-31 ± 3

Arrhenius Plots

The Arrhenius equation relates the rate constant to the temperature and activation energy of the dependence of reaction rates, as given in Equation 1. *k* is the rate constant at an absolute temperature, T, A is the pre-exponential factor, E_a is the activation energy and R is the ideal gas constant.[3] Taking the natural logarithm of the Arrhenius equation yields Equation 2.

$$k = Ae^{\frac{-Ea}{RT}} \quad (1)$$

$$ln\ k = ln\ A\ - \frac{E_a}{R}\frac{1}{T} \quad (2)$$

The activation energy (E_a) was obtained by converting the slope of the fit using the ideal gas constant, and the pre-exponential factor (A) was calculated by taking the anti-log of the intercept.

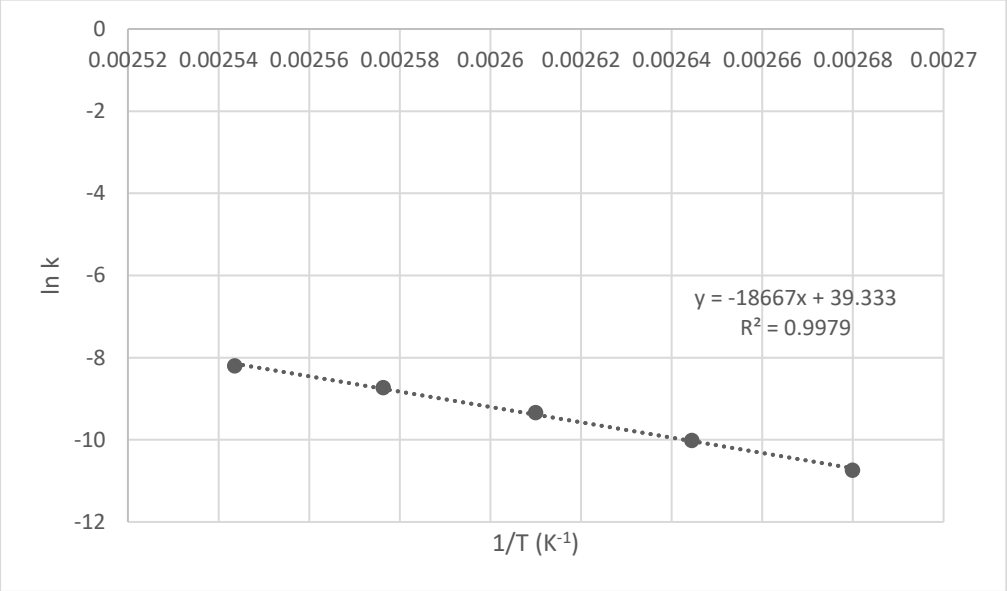


Figure S4. Arrhenius plot of ln k versus 1/T for reactions performed in $[C_4C_1im][NTf_2]$.

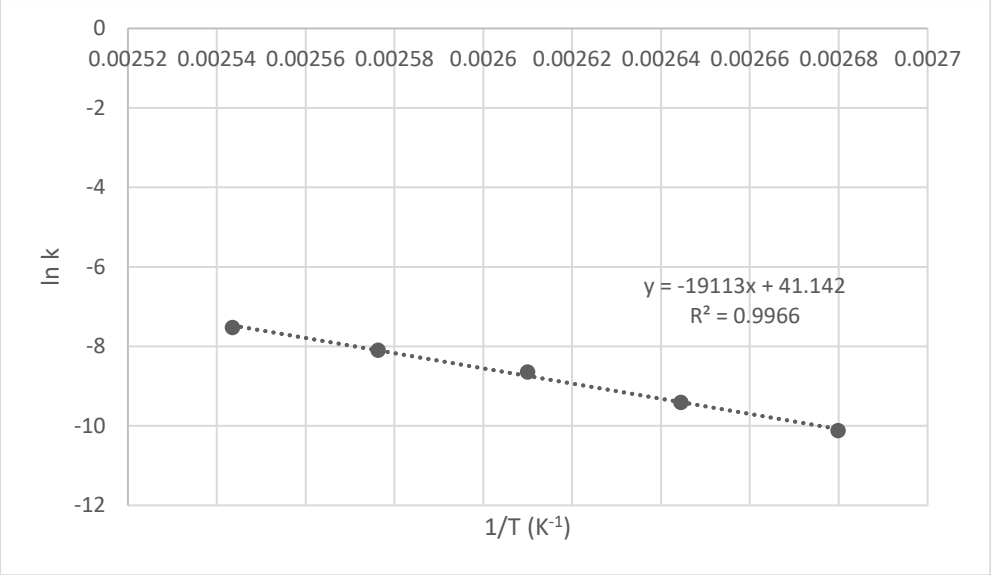


Figure S5. Arrhenius plot of ln k versus 1/T for reactions performed in $[C_{10}C_1im][NTf_2]$.

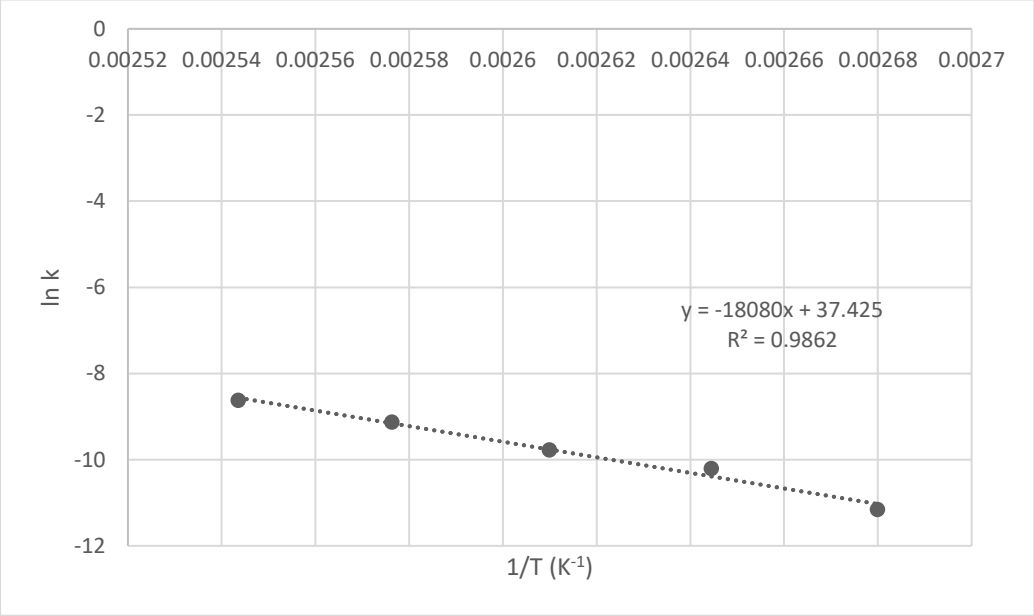


Figure S6. Arrhenius plot of ln k versus 1/T for reactions performed in $[C_4C_1im][OTf]$.

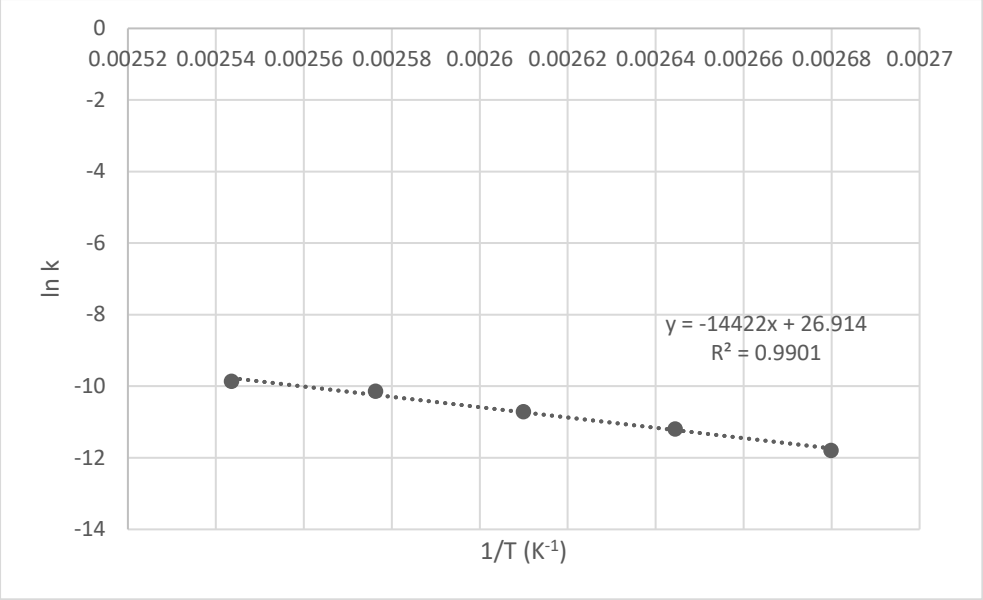


Figure S7. Arrhenius plot of ln k versus 1/T for reactions performed in $[C_{10}C_1im][OTf]$.

Eyring Plots

The Eyring equation, given in Equation 3, relates the change in rate constants with temperature to the thermodynamic parameters of the initial and transition states. This equation allows for the specific role of changing the solvent on the reaction mechanism to be identified.[3] *k* is the rate constant at an absolute temperature, T, k_B is Boltzmann's constant, h is Planck's constant, κ is the transmission coefficient, R is the ideal gas constant and $\Delta^{\ddagger}G^{\Theta}$ is the Gibb's energy of activation.[3] This equation can be rewritten to yield Equation 4, where $\Delta^{\ddagger}H^{\Theta}$ is the enthalpy of activation and $\Delta^{\ddagger}S^{\Theta}$ is the entropy of activation.

$$k = \frac{\kappa k_B T}{h} e^{\frac{-\Delta^{\ddagger}G^{\theta}}{RT}} \quad (3)$$

$$ln\frac{k}{T} = \frac{-\Delta^{\ddagger}H^{\Theta}}{R} \cdot \frac{1}{T} + ln\frac{\kappa k_B}{h} + \frac{\Delta^{\ddagger}S^{\Theta}}{R} \quad (4)$$

The activation enthalpy ($\Delta^{\ddagger}H$) was calculated by converting the slope of the fit using the ideal gas constant, and the activation entropy ($\Delta^{\ddagger}S$) was obtained by multiplying the intercept by the ideal gas constant and subtracting $\ln(k_B/h)$. The transmission coefficient (κ) was assumed to be 1.

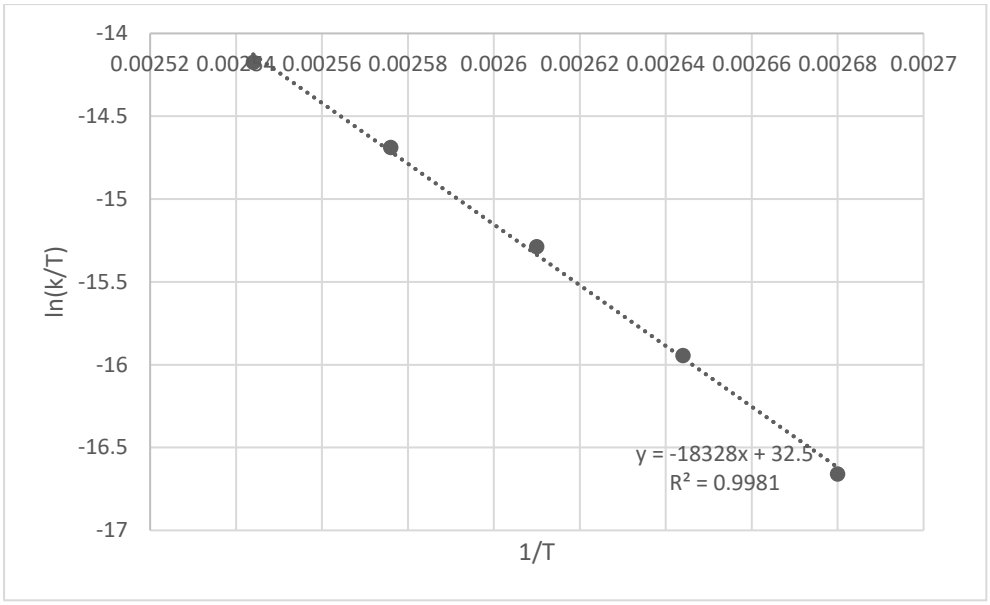


Figure S8. Eyring plot for dehydration reaction of decahydro-2-naphthol performed in $[C_4C_1im][NTf_2]$.

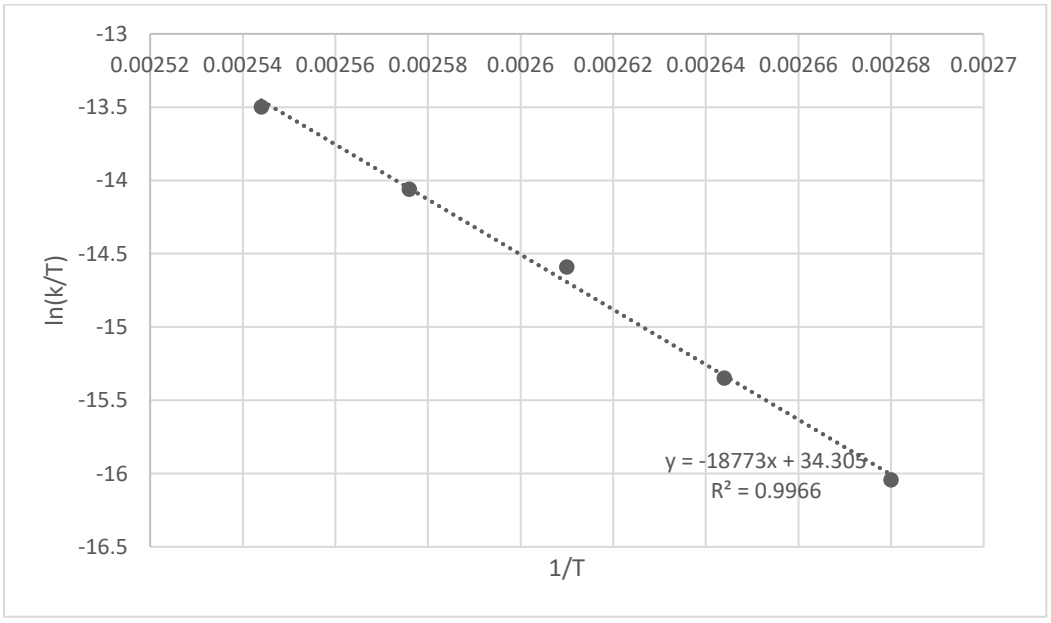


Figure S9. Eyring plot for dehydration reaction of decahydro-2-naphthol performed in $[C_{10}C_1im][NTf_2]$.

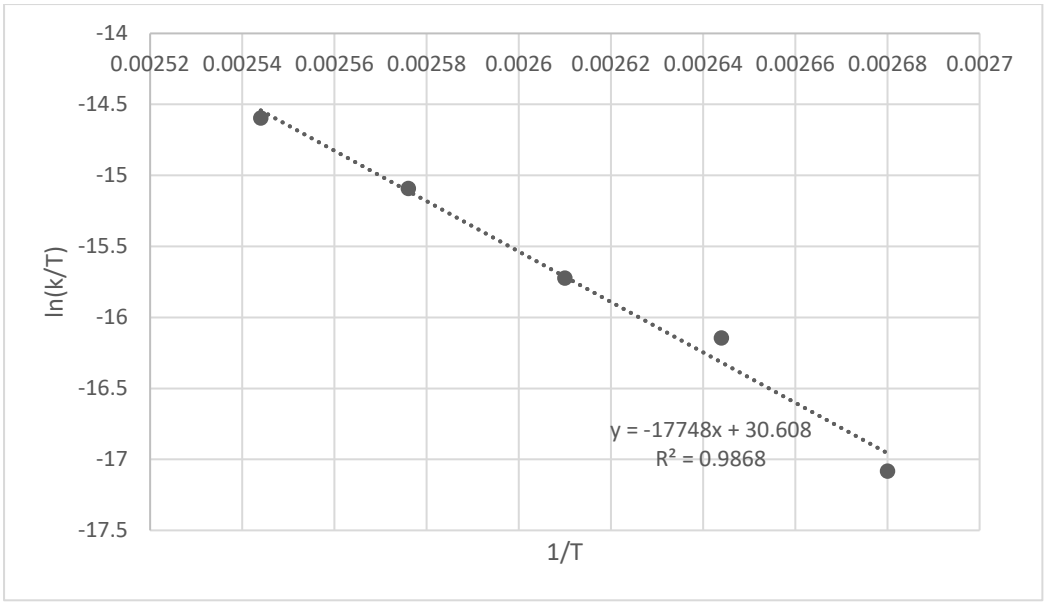


Figure S10. Eyring plot for dehydration reaction of decahydro-2-naphthol performed in [C_4C_1im][OTf].

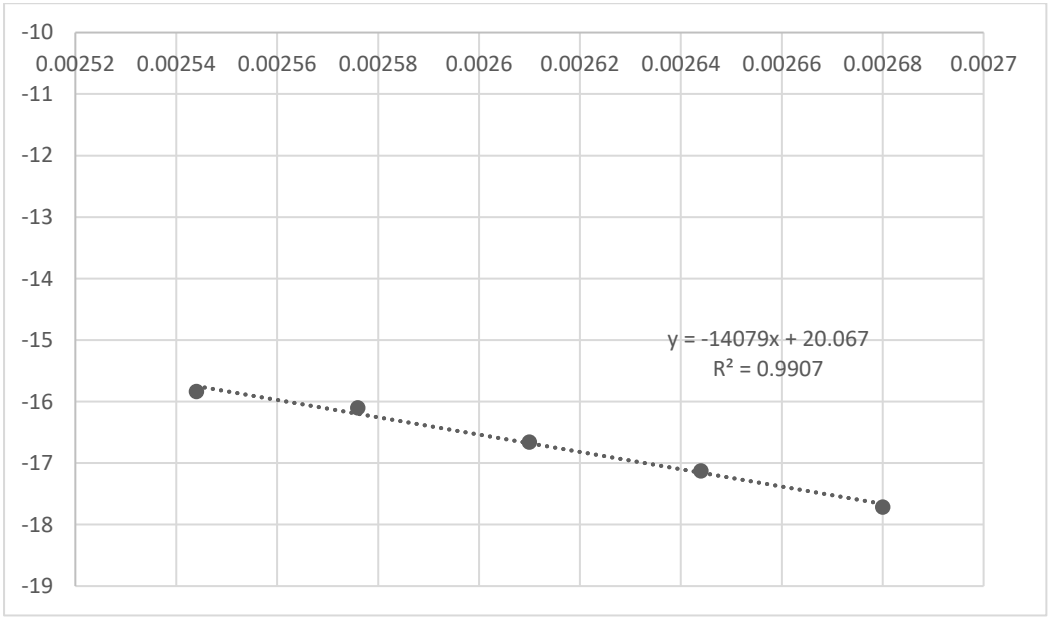


Figure S11. Eyring plot for dehydration reaction of decahydro-2-naphthol performed in [$C_{10}C_1$im][OTf].

Acidity of p-TSA in ILs

Table S5. Difference in chemical shift (Δδ) between the α and β carbon signals of mesityl oxide in ILs containing p-toluenesulfonic acid and the calculated Hammett acidity (H_0).

Ionic Liquid	Δδ	H_0
$[C_4C_1im][OTf]$	30.9	-
$[C_{10}C_1im][OTf]$	30.4	-
$[C_4C_1im][NTf_2]$	36.6	-1.9
$[C_{10}C_1im][NTf_2]$	35.8	-1.7

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2. J. Gräsvik, J. P. Hallett, T. Q. To and T. Welton, *Chem. Commun.*, 2014, **50**, 7258-7261.
3. R. G. Mortimer, *Physical Chemistry*, Harcourt/Academic Press, San Diego, 2000.