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Thermal decomposition of carboxylate ionic liquids: trends and mechanisms

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Electronic Supplementary Information

1. General Laboratory Procedures

All reactions requiring an inert atmosphere were performed under a blanket of nitrogen gas, which was dried through a column of phosphorus pentoxide. All commercially acquired chemicals were obtained from Sigma-Aldrich, and were used without further purification unless otherwise stated. Anhydrous solvents were dried through an HPLC column on an Innovative Technology Inc. solvent purification system. NMR spectra were recorded on Bruker Avance-400 (^{1}H NMR (400 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz)) NMR spectrometers. Chemical shifts are reported in ppm (relative to the DMSO-d6 residual peak). IR spectra were recorded on a Perkin Elmer spectrum 100 FTIR using an ATR inset with a diamond crystal. LSIMS mass spectrometry was performed on a Micromass AutoSpec Premier mass spectrometer. Melting point measurements were carried out on a Stanford Research Systems 'OptiMelt' automated melting point system, with a heating rate of 1 ^{o}C min^{-1}. Melting point values are uncorrected. Elemental analysis experiments were carried out by the London Metropolitan University service.

2. Synthesis of Ionic Liquid Compounds

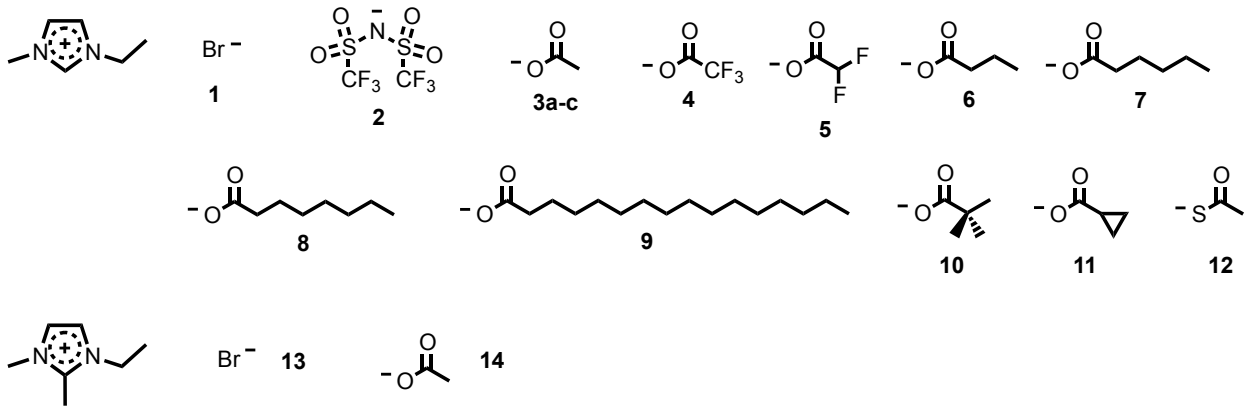


Fig E1: Ionic liquids synthesised in this investigation, incorporating the 1-ethyl-3-methylimidazolium, $[C_2C_1im]^+$, cation (**1-12**) and 1-ethyl-2,3-dimethylimidazolium, $[C_2C_1C_1im]^+$, cation (**13** and **14**).

1-Ethyl-3-methylimidazolium bromide (**1**)**.** Freshly distilled bromoethane (190 ml, 2.50 mol) was added dropwise (slowly) to freshly distilled 1-methylimidazole (190 ml, 2.38 mol) overnight, under a nitrogen atmosphere and with vigorous stirring. During this time, a white solid formed. The solid was recrystallised from 60:40 MeCN / EtOAc (300 ml), and the residual solution was carefully decanted off. The solid was washed with Et_2O (3 x 150 ml), and was recrystallised a further time from 80:20 MeCN / EtOAc (300 ml). The residual solution was carefully decanted off, and the solid was dried under vacuum to yield 1-ethyl-3-methylimidazolium bromide (279 g, 61%) as a white crystalline solid.
Found: m.p. 70.0 - 72.0 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d6): δ 9.16 (1H, s), 7.80 (1H, t, J = 2 Hz), 7.71 (1H, t, J = 2 Hz), 4.19 (2H, q, J = 7 Hz), 3.85 (3H, s), 1.41 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 136.2, 123.5, 122.0, 44.1, 35.7, 15.1. *ν*(neat)/cm^{-1} 3143 3070 (aromatic C-H stretch, m), 2987 (aliphatic C-H stretch, m), 1570 (arom. ring def., m). m/z (LSIMS^{+}): 111 (100%) $[C_2C_1im]^+$. m/z (LSIMS^{-}): 46 (100%) $[EtOH]^-$, 80 (83%) $[H\text{-}Br]^-$, 81 (48%) $[^{81}Br]^-$, 79 (47%) $[^{79}Br]^-$. Calc. for $C_6H_{11}BrN_2$: C, 37.72; H, 5.80; N, 14.66%. Found: C, 37.69; H, 5.82; N, 14.52%.

1-Ethyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (**2**). 1-Ethyl-3-methylimidazolium bromide (**1**) (25.0 g, 130 mmol) and lithium *bis*(trifluoromethanesulfonyl)imide (40.0 g, 139 mmol) were weighed into a 250 ml round-bottomed flask, and deionized water (100 ml) was added. The solution was stirred at room temperature for 2 h, during which time a biphasic solution had formed. The solution was transferred into a separating funnel, and the layers were separated. The lower ionic liquid layer was washed with deionized water (2 x 75 ml) and dried under vacuum at 50 ^{o}C overnight, to yield 1-ethyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (42.6 g, 83%) as a colourless liquid.

Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 8.10 (1H, s), 7.77 (1H, t, J = 2 Hz), 7.68 (1H, t, J = 2 Hz), 4.18 (2H, q, J = 8 Hz), 3.84 (3H, s), 1.41 (3H, t, J = 8 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 136.2, 123.6, 122.0, 119.5, 44.1, 35.7, 15.1. ^{19}F NMR (376 MHz, DMSO-d6): δ -100.0. *ν*(neat)/cm^{-1} 3159 (aromatic C^{4}-H / C^{5}-H stretch, m), 3127 (aromatic C^{2}-H stretch, m), 2995 (aliphatic C-H stretch, m), 1576 (arom. ring def., m), 1330 (asym. S=O stretch, s), 1132 (sym. S=O stretch, m).[1] m/z (ES^{+}): 111 (100%) [C_2C_1im]$^{+}$. m/z (ES^{-}): 280 (100%) [NTf_2]$^{-}$. Calc. for $C_8H_{11}F_6N_3O_4S_2$: C, 24.55; H, 2.83; N, 10.74%. Found: C, 24.61; H, 2.86; N, 10.75%.

1-Ethyl-3-methylimidazolium acetate (**3a**)**.** 1-Ethyl-3-methylimidazolium bromide (**1**) (15.00 g, 79 mmol) and silver acetate (13.17 g, 79 mmol) were carefully weighed into a 100 ml round-bottomed flask, and the flask was wrapped in aluminium foil to prevent photodegradation of the silver acetate. Deionized water (50 ml) was added, and the solution was stirred at room temperature for three days, during which time a yellow/green precipitate formed. The solution was filtered through a sintered glass funnel. The solution was tested for the presence of excess Ag^{+} or Br^{-} as follows: one or two drops of the impure aqueous ionic liquid solution were added to two glass vials, and both were diluted with deionized water (1 ml). To the first vial was added a few drops of 1M aqueous HCl, and to the other a few drops of 1M aqueous silver nitrate. The tests indicated that there was a slight excess of Ag^{+}. Aqueous solutions of 1-ethyl-3-methylimidazolium bromide and silver acetate were added dropwise to the acetate ionic liquid, alternately with stirring, until no further precipitate formation was observed. The opaque solution was filtered, giving a colourless, clear solution, which tested negative with both 1M aqueous HCl and 1M aqueous silver nitrate. The water was removed by rotary evaporation, and the product was dried at 50 °C under vacuum, to give 1-ethyl-3-methylimidazolium acetate (11.40 g, 85%) as a colourless viscous liquid.
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.98 (1H, s), 7.86 (1H, t, J = 2 Hz), 7.77 (1H, t, J = 2 Hz), 4.21 (2H, q, J = 8 Hz), 3.87 (3H, s), 1.55 (3H, s), 1.40 (3H, t, J = 8 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 172.6, 137.2, 123.5, 121.9, 44.0, 35.6, 26.4, 15.2. *ν*(neat)/cm^{-1} 3147 3072 (aromatic C-H stretch, w), 2981 (aliphatic C-H stretch, m), 1559 (C=O stretch, s). m/z (LSIMS^{+}): 111 (100%) [C_2C_1im]$^{+}$, 83 (68%) [C_1Him]$^{+}$, 69 (8%) [H_2im]$^{+}$. m/z (LSIMS^{-}): 27 (100%), 36 (93%), 80 (12%) [Na-OAc]$^{-}$, 59 (8%) [OAc]$^{-}$.

1-Ethyl-3-methylimidazolium acetate (compound **3c**). The ionic liquid was acquired from BASF Basionics© as a red viscous liquid, and used as received.
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.96 (1H, s), 7.85 (1H, t, J = 2 Hz), 7.76 (1H, t, J = 2 Hz), 4.21 (2H, q, J = 8 Hz), 3.86 (3H, s), 1.55 (3H, s), 1.40 (3H, t, J = 8 Hz). *ν*(neat)/cm^{-1} 3141 3034 (aromatic C-H stretch, w), 2975 (aliphatic C-H stretch, m), 1559 (C=O stretch, s).

General Procedure for 1-Ethyl-3-methylimidazolium carboxylate ionic liquids (**3b, 4-11**):

Barium hydroxide octahydrate (1 equiv.) was added to deionized water (10 ml per 1 g of barium hydroxide octahydrate), and the solution was heated at 70 °C for 1 h. Separately, 1-ethyl-3-methylimidazolium hydrogen sulfate (**14**) (1 equiv.) was diluted with an equal volume of deionized water, and this aqueous solution was added dropwise to the hot aqueous barium hydroxide solution over five minutes, whereupon a white precipitate formed. The mixture was heated at 70 °C for a further 1 h. The mixture was cooled to room temperature and refrigerated for a minimum of 30 minutes, to encourage all barium sulfate to precipitate out. The cold solution was filtered, generating an aqueous solution of 1-ethyl-3-methylimidazolium hydroxide. This basic solution was treated with the conjugate carboxylic acid H[A] (1 equiv.), until the pH of the solution had reached ca. 7. The water was removed by rotary evaporation and the ionic liquid was filtered to remove small quantities of solid material. The ionic liquid was dried under high vacuum at 50 °C.

1-Ethyl-3-methylimidazolium acetate (**3b**). In addition to the above procedure, the coloured product was treated with decolorizing charcoal, and stirred at 50 °C for three days. The solution was cooled to room temperature, and the product was filtered through silica to remove the charcoal. The product was dried under high vacuum to yield 1-ethyl-3-methylimidazolium acetate (14.3 g, 70%) as a colourless viscous liquid.
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.90 (1H, s), 7.84 (1H, t, J = 2 Hz), 7.75 (1H, t, J = 2 Hz), 4.21 (2H, q, J = 7 Hz), 3.86 (3H, s), 1.54 (3H, s), 1.40 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 172.8, 137.3, 123.5, 121.9, 44.0, 35.5, 26.3, 15.2. *ν*(neat)/cm^{-1} 3144 3043 (aromatic C-H stretch, w), 2977 (aliphatic

C-H stretch, m), 1559 (C=O stretch, s). m/z (LSIMS$^+$): 111 (100%) $[C_2C_1im]^+$, 83 (4%) $[C_1Him]^+$. m/z (LSIMS$^-$) : 59 (100%) $[OAc]^-$. Calc. for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46%. Found: C, 56.33; H, 8.27; N, 16.39%.

1-Ethyl-3-methylimidazolium trifluoroacetate (**4**). The product was collected as a pale yellow viscous liquid (4.04 g, 75%).
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.16 (1H, s), 7.79 (1H, t, J = 2 Hz), 7.71 (1H, t, J = 2 Hz), 4.19 (2H, q, J = 7 Hz), 3.84 (3H, s), 1.41 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 136.3, 123.6, 122.0, 118.9, 115.9, 44.1, 35.7, 15.1. ^{19}F NMR (376 MHz, DMSO-d6): δ -73.4. *v*(neat)/cm^{-1} 3154 3085 (aromatic C-H stretch, w), 2993 (aliphatic C-H stretch, m), 1683 (C=O stretch, s), 1574 (arom. ring def., m). m/z (LSIMS$^+$): 111 (100%) $[C_2C_1im]^+$, 83 (4%) $[C_1Him]^+$. m/z (LSIMS$^-$): 113 (100%) $[CF_3CO_2]^-$, 69 (9%) $[CF_3]^-$. Calc. for $C_8H_{11}F_3N_2O_2$: C, 42.86; H, 4.95; N, 12.50%. Found: C, 41.96; H, 5.09; N, 12.43%.

1-Ethyl-3-methylimidazolium difluoroacetate (**5**). The product was collected as a colourless viscous liquid (3.37 g, 43%).
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.30 (1H, s), 7.79 (1H, t, J = 2 Hz), 7.71 (1H, t, J = 2 Hz), 5.49 (1H, t, J = 55 Hz), 4.19 (2H, q, J = 7 Hz), 3.85 (3H, s), 1.41 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 137.0, 124.0, 122.4, 111.1, 44.5, 36.1, 15.6. ^{19}F NMR (376 MHz, DMSO-d6): δ -120.8. *v*(neat)/cm^{-1} 3148 3073 (aromatic C-H stretch, w), 2984 (aliphatic C-H stretch, m), 1640 (C=O stretch, s), 1570 (arom. ring def., m). m/z (LSIMS$^+$): 111 (100%) $[C_2C_1im]^+$, 83 (41%) $[C_1Him]^+$, 69 (16%) $[H_2im]^+$. m/z (LSIMS$^-$): 95 (100%) $[CHF_2CO_2]^-$. Calc. for $C_8H_{12}F_2N_2O_2$: C, 46.60; H, 5.87; N, 13.59%. Found: C, 46.53; H, 5.96; N, 13.52%.

1-Ethyl-3-methylimidazolium butyrate (**6**). The product was collected as a pale yellow odiferous viscous liquid (14.02 g, 74%).
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.79 (1H, s), 7.82 (1H, t, J = 2 Hz), 7.73 (1H, t, J = 2 Hz), 4.20 (2H, q, J = 8 Hz), 3.86 (3H, s), 1.75 (2H, t, J = 8 Hz), 1.44-1.32 (5H, m), 0.78 (3H, t, J = 8 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 175.1, 137.4, 123.5, 121.9, 44.0, 41.4, 35.5, 19.9, 15.2, 14.6. *v*(neat)/cm^{-1} 3147 3070 (aromatic C-H stretch, w), 2958 2871 (aliphatic C-H stretch, m), 1557 (C=O stretch, s). m/z (LSIMS$^+$): 111 (100%) $[C_2C_1im]^+$, 83 (6%) $[C_1Him]^+$. m/z (LSIMS$^-$): 87 (100%) $[CH_3(CH_2)_2CO_2]^-$. Calc. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13%. Found: C, 60.40; H, 9.26; N, 14.01%.

1-Ethyl-3-methylimidazolium hexanoate (**7**). The product was collected as a yellow viscous liquid (0.70 g, 26%).
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.69 (1H, s), 7.81 (1H, t, J = 2 Hz), 7.72 (1H, t, J = 2 Hz), 4.20 (2H, q, J = 8 Hz), 3.86 (3H, s), 1.75 (2H, t, J = 8 Hz), 1.45-1.31 (5H, m), 1.28-1.09 (4H, m), 0.83 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 175.0, 137.1, 123.5, 121.9, 44.0, 35.6, 32.0, 26.5, 26.2, 22.3, 15.2, 14.1. *v*(neat)/cm^{-1} 3141 3071 (aromatic C-H stretch, m), 2956 2930 2873 2859 (aliphatic C-H stretch, w), 1558 (C=O stretch, s). m/z (LSIMS$^+$): 111 (100%) $[C_2C_1im]^+$, 83 (6%) $[C_1Him]^+$. m/z (LSIMS$^-$): 115 (100%) $[CH_3(CH_2)_4CO_2]^-$.

1-Ethyl-3-methylimidazolium octanoate (**8**). The product was collected as a pale yellow viscous liquid (6.20 g, 51%).
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.69 (1H, s), 7.81 (1H, t, J = 1 Hz), 7.72 (1H, t, J = 1 Hz), 4.20 (2H, q, J = 7 Hz), 3.86 (3H, s), 1.75 (2H, t, J = 7 Hz), 1.45-1.31 (5H, m), 1.30-1.11 (8H, m), 0.85 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 175.0, 137.1, 123.5, 121.9, 44.0, 35.6, 31.5, 29.6, 28.9, 26.8, 22.2, 15.2, 14.0. *v*(neat)/cm^{-1} 3147 3057 (aromatic C-H stretch, m), 2957 2924 2873 2854 (aliphatic C-H stretch, w), 1559 (C=O stretch, s). m/z (LSIMS$^+$): 111 (100%) $[C_2C_1im]^+$, 83 (37%) $[C_1Him]^+$, 69 (31%) $[H_2im]^+$. m/z (LSIMS$^-$): 143 (100%) $[CH_3(CH_2)_6CO_2]^-$.

1-Ethyl-3-methylimidazolium palmitate (**9**). Due to the surfactant behaviour of the palmitate anion, rotary evaporation of the water was difficult. Instead, a small quantity of the product precipitated out of the aqueous solution overnight. The product was collected as a white waxy solid (0.5 g, 6%).
Found: m.p. 47.0 - 49.0 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d6): δ. ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 136.7, 123.6, 122.0, 44.1, 35.7, 31.3, 29.2, 29.2, 29.1, 29.1, 28.8, 22.1, 15.2, 14.0. *v*(neat)/cm^{-1} 3150 3092 (aromatic C-H stretch, w), 2956 2916 2849 (aliphatic C-H stretch, s), 1563 (C=O stretch, s). m/z (LSIMS$^+$):

111 (100%) $[C_2C_1im]^+$, 88 (39%), 83 (30%) $[C_1Him]^+$, 69 (19%) $[H_2im]^+$. m/z (LSIMS$^-$): 255 (100%) $[CH_3(CH_2)_{14}CO_2]^-$. Calc. for $C_{22}H_{42}N_2O_2$: C, 72.08; H, 11.55; N, 7.64%. Found: C, 71.95; H, 11.60; N, 7.54%.

1-Ethyl-3-methylimidazolium pivalate (**10**). The product was collected as a colourless, highly viscous liquid, which partially solidified upon cooling (3.77 g, 53%).
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.79 (1H, s), 7.82 (1H, t, J = 2 Hz), 7.73 (1H, t, J = 2 Hz), 4.21 (2H, q, J = 8 Hz), 3.86 (3H, s), 1.41 (3H, t, J = 7 Hz), 0.93 (9H, s). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 137.2, 123.5, 121.9, 109.5, 44.0, 38.6, 35.6, 29.3, 15.2. *v*(neat)/cm^{-1} 3144 3057 (aromatic C-H stretch, w), 2946 2861 (aliphatic C-H stretch, m), 1552 (C=O stretch, s). m/z (LSIMS$^+$): 111 (100%) $[C_2C_1im]^+$ 83 (5%) $[C_1Him]^+$. m/z (LSIMS$^-$): 101 (100%) $[C(CH_3)_3CO_2]^-$. Calc. for $C_{11}H_{20}N_2O_2$: C, 62.23; H, 9.50; N, 13.20%. Found: C, 62.13; H, 9.62; N, 13.18%.

1-Ethyl-3-methylimidazolium cyclopropanecarboxylate (**11**). The product was collected as a pale yellow highly viscous liquid (8.46 g, 90%).
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.68 (1H, s), 7.81 (1H, s), 7.72 (1H, s), 4.20 (2H, q, J = 7 Hz), 3.86 (3H, s), 1.40 (3H, t, J = 7 Hz), 1.01 (1H, m), 0.38 (2H, m), 0.22 (2H, m). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 175.4, 137.0, 123.5, 121.9, 44.0, 35.6, 16.3, 15.2, 5.1. *v*(neat)/cm^{-1} 3140 (aromatic C-H stretch, w), 3003 2867 (aliphatic C-H stretch, m), 1555 (C=O stretch, s). m/z (LSIMS$^+$): 133 (100%) $[C_2C_1im + Na]^+$, 111 (8%) $[C_2C_1im]^+$. m/z (LSIMS$^-$): 85 (100%) $[(c\text{-}C_3H_5)CO_2]^-$. Calc. for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.27%. Found: C, 61.09; H, 8.35; N, 14.19%.

Modified Procedure for 1-Ethyl-3-methylimidazolium thioacetate (**12**)**:**

1-Ethyl-3-methylimidazolium thioacetate (**12**). The procedure was identical as for ionic liquids **3b, 4-11** up to and including the point of removing the barium sulfate by filtration. Additional measures were then taken to prevent hydrolysis of the thioacetate anion:

The aqueous solution of 1-ethyl-3-methylimidazolium hydroxide was reduced to approximately 25% of the original volume by rotary evaporation of water. The concentrated basic solution was cooled to approximately 0 ^{o}C in an ice bath, and was treated with thioacetic acid (ca. 1.83 g, 24 mmol), until the pH of the solution had reached ca. 7. The remaining water was removed under high vacuum, and the ionic liquid was filtered to remove small quantities of solid material. The ionic liquid was further dried under high vacuum at room temperature. The product was collected as a yellow odiferous viscous liquid (3.30 g, 74%), and was stored at 4 ^{o}C.
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.26 (1H, s), 7.80 (1H, s), 7.71 (1H, s), 4.20 (2H, q, J = 7 Hz), 3.85 (3H, s), 2.11 (3H, s), 1.41 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 211.5, 136.4, 123.5, 121.9, 44.1, 35.7, 15.1. *v*(neat)/cm^{-1} 3144 3063 (aromatic C-H stretch, w), 2979 2873 (aliphatic C-H stretch, m), 1531 (C=O stretch, s). m/z (LSIMS$^+$): 111 (100%) $[C_2C_1im]^+$, 83 (14%) $[C_1Him]^+$, 69 (25%) $[H_2im]^+$. m/z (LSIMS$^-$): 75 (100%) $[SAc]^-$.

Synthesis of 1-Ethyl-2,3-dimethylimidazolium Ionic Liquids (**13** and **14**):

1-Ethyl-2,3-dimethylimidazolium bromide (**13**). Freshly distilled 1,2-dimethylimidazole (18.50 g, 192 mmol) was diluted in dry toluene (150 ml) in a three-necked 500 ml round-bottomed flask fitted with a dropping funnel and a thermometer. The dropping funnel was charged with freshly distilled bromoethane (21.9 g, 201 mmol). The bromoethane was added dropwise to the toluene solution over 20 minutes with vigorous stirring, at room temperature and under a nitrogen atmosphere. The solution was stirred vigorously overnight. During this time, a white solid formed. The solution was allowed to settle, and the solvent was carefully decanted off. The white solid was washed with toluene (3 x 100 ml), and was dried under high vacuum. The crude product was recrystallised from 50:50 MeCN / EtOAc (250 ml) to yield 1-ethyl-2,3-dimethylimidazolium bromide (7.3 g, 18%) as a white crystalline solid.
Found: m.p. 138 - 140 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d6): δ 7.69 (1H, d, J = 2 Hz), 7.65 (1H, d, J = 2 Hz), 4.15 (2H, q, J = 8 Hz), 3.75 (3H, s), 2.59 (3H, s), 1.33 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6):

δ 144.1, 122.4, 120.3, 42.8, 34.7, 14.9, 9.1. *v*(neat)/cm^{-1} 3445, 3383 (aromatic C-H stretch, m), 3120 3092 (aliphatic C-H stretch, w). m/z (LSIMS$^+$): 125 (100%) [$C_2C_1C_1im$]$^+$, 97 (18%) [C_1C_1Him]$^+$. m/z (LSIMS$^-$): 81 (100%) [^{81}Br]$^-$, 79 (94%) [^{79}Br]$^-$. Calc. for $C_7H_{13}BrN_2$: C, 40.99; H, 6.39; N, 13.66%. Found: C, 40.92; H, 6.50; N, 13.74%.

1-Ethyl-2,3-dimethylimidazolium acetate (**14**). 1-Ethyl-2,3-dimethylimidazolium bromide (**13**) (4.00 g, 19 mmol) and silver(I) acetate (3.25 g, 19 mmol) were carefully weighed into a 100 ml round-bottomed flask, and the flask was wrapped in aluminium foil to prevent photodegradation of the silver(I) acetate. Deionized water (60 ml) was added, and the solution was stirred at room temperature overnight, during which time a yellow/green precipitate formed. The solution was filtered, giving a colourless, clear solution. The water was removed by rotary evaporation, and the product was dried at 50 °C under vacuum to give a pale yellow viscous liquid that solidified upon cooling. The crude product was recrystallised from 50:50 MeCN / EtOAc (12 ml) to yield 1-ethyl-2,3-dimethylimidazolium acetate (1.12 g, 31%) as an off-white crystalline solid.
Found: m.p. 90.0 - 92.0 °C. ^{1}H NMR (400 MHz, DMSO-d6): δ 7.74 (1H, d, J = 2 Hz), 7.70 (1H, d, J = 2 Hz), 4.15 (2H, q, J = 7 Hz), 3.76 (3H, s), 2.59 (3H, s), 1.48 (3H, s), 1.32 (3H, t, J = 7 Hz, f). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 172.0, 144.0, 122.5, 120.4, 42.7, 34.6, 26.5, 14.9, 9.0. *v*(neat)/cm^{-1} 3135 (aromatic C-H stretch, m), 2982 (aliphatic C-H stretch, m), 1567 (C=O stretch, s). m/z (LSIMS$^+$): 125 (100%) [$C_2C_1C_1im$]$^+$, 97 (19%) [C_1C_1Him]$^+$. m/z (LSIMS$^-$): 59 (100%) [OAc]$^-$.

Synthesis of Intermediate Ionic Liquids (**15** and **16**)**:**

1-Ethyl-3-methylimidazolium methyl sulfate (**15**). Freshly distilled 1-ethylimidazole (79.6 g, 828 mmol) was diluted with dry toluene (300 ml) in a three-necked round-bottomed flask fitted with a dropping funnel, thermometer and nitrogen line. Freshly distilled dimethyl sulfate (100.7 g, 798 mmol) was added dropwise over seven hours, under a nitrogen atmosphere, during which time a biphasic solution had formed. The solution was stirred at room temperature overnight, under a nitrogen atmosphere. The layers were separated, and the lower layer was washed with toluene (3 x 25 ml). The ionic liquid was dried under high vacuum to yield 1-ethyl-3-methylimidazolium methyl sulfate (171.1 g, 96%) as a colourless viscous liquid.
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.11 (1H, s), 7.78 (1H, s), 7.69 (1H, s), 4.19 (2H, q, J = 7 Hz), 3.84 (3H, s), 3.37 (3H, s), 1.41 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 136.3, 123.6, 122.0, 52.8, 44.1, 35.7, 15.1. *v*(neat)/cm^{-1} 3152 3107 (aromatic C-H stretch, m), 2988 2948 2833 (aliphatic C-H stretch, w), 1573 (arom. ring def., m), 1215 (asym. S=O stretch, s) 1003 (sym. S=O stretch, s). m/z (LSIMS$^+$): 111 (100%) [C_2C_1im]$^+$, 83 (59%) [C_1Him]+, 69 (9%) [H_2im]$^+$. m/z (LSIMS$^-$): 147 (100%), 111 (21%) [$MeSO_4$]$^-$. Calc. for $C_7H_{14}N_2O_4S$: C, 37.83; H, 6.35; N, 12.60%. Found: C, 37.69; H, 6.38; N, 12.52%.

1-Ethyl-3-methylimidazolium hydrogen sulfate (**16**).[2] 1-Ethyl-3-methylimidazolium methyl sulfate (**15**) (57.5 g, 258 mmol) was diluted with deionized water (5 ml) in an open-topped three-necked round-bottomed flask fitted with dropping funnel and thermometer. Aqueous 5M sulphuric acid (2 drops) was added. The solution was heated at 175 °C for 3 h with vigorous stirring, allowing water and generated methanol to boil off. Deionized water was dispensed dropwise from the dropping funnel, in order to maintain the temperature of 175 °C. The solution was allowed to cool to room temperature, deionized water (50 ml) and decolorizing charcoal were added, and the slurry was stirred at 50 °C overnight. The slurry was filtered through silica gel, and the water was removed by rotary evaporation. The product was dried under high vacuum to yield 1-ethyl-3-methylimidazolium hydrogen sulfate (53.0 g, 98%) as a colourless highly-viscous liquid.
Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.15 (1H, s), 7.79 (1H, s), 7.70 (1H, s), 4.19 (2H, q, J = 7 Hz), 3.84 (3H, s), 1.40 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 136.4, 123.6, 122.0, 44.1, 35.7, 15.2. *v*(neat)/cm^{-1} 3151 3106 (aromatic C-H stretch, m), 2984 (aliphatic C-H stretch, m), 1572 (arom. ring def., m), 1160 (asym. S=O stretch, s) 1021 (sym. S=O stretch, s) m/z (LSIMS$^+$): 111 (100%) [C_2C_1im]$^+$, 83 (80%) [C_1Him]$^+$, 69 (9%) [H_2im]$^+$. m/z (LSIMS$^-$): 97 (100%) [HSO_4]$^-$. Calc. for $C_6H_{12}N_2O_4S$: C, 34.61; H, 5.81; N, 13.45%. Found: C, 34.53; H, 5.84; N, 13.57%.

3. Thermogravimetric Analysis (TGA) Procedures

Thermogravimetric Analysis (TGA) spectra were obtained on a PerkinElmer 'Pyris 1 TGA' Thermogravimetric Analyzer, using platinum sample pans of 6 mm diameter.

Scanning TGA experiments were carried out for compounds **1-14** in the range of 25 - 700 ^{o}C. Between 4 - 8 mg of the ionic liquid was measured into the platinum pan. Ionic liquids were dried thoroughly under high vacuum prior to TGA measurement. However, during the transferal of the hygroscopic ionic liquid into the TGA pan, a small quantity of water (≤ 5 weight %) would be absorbed from the atmosphere. A **drying procedure** was therefore implemented: the ionic liquid was heated to 80 ^{o}C for 30 minutes in the TGA apparatus, in order to remove water.* The compound was then cooled to room temperature before resetting the sample weight and starting the scan. This drying procedure was not necessary for the hydrophobic ionic liquid 1-ethyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide, **2**. A ramping rate of 10 ^{o}C min^{-1} and a nitrogen flow of 20 ml min^{-1} were used for scanning experiments, unless otherwise indicated. Experiments were performed in triplicate. For all ionic liquids in the series, the T_{onset} temperatures for the repeat experiments fall within ± 2 ^{o}C of the original measurement for each compound:

Table E1: T_{onset} values for thermal decomposition of ionic liquids **1-14**. Temperature-ramped TGA experiments were performed with a heating rate of 10 ^{o}C min^{-1}, using nitrogen carrier gas.

	Ionic Liquid	T_{onset} Exp. 1 (°C)	T_{onset} Exp. 2 (°C)	T_{onset} Exp. 3 (°C)
1	$[C_2C_1im]Br$	301	300	302
2	$[C_2C_1im][NTf_2]$	436	436	434
3a	$[C_2C_1im][OAc]$ Ag Route	214	216	213
3b	$[C_2C_1im][OAc]$ Ba Route	216	214	217
3c	$[C_2C_1im][OAc]$ Commercial	216	215	217
4	$[C_2C_1im][CF_3CO_2]$	172	170	173
5	$[C_2C_1im][CHF_2CO_2]$	263	263	264
6	$[C_2C_1im][CH_3(CH_2)_2CO_2]$	213	211	214
7	$[C_2C_1im][CH_3(CH_2)_4CO_2]$	212	210	213
8	$[C_2C_1im][CH_3(CH_2)_6CO_2]$	216	211	213
9	$[C_2C_1im][CH_3(CH_2)_{14}CO_2]$	216	217	214
10	$[C_2C_1im][C(CH_3)_3CO_2]$	212	211	213
11	$[C_2C_1im][c\text{-}(C_3H_5)CO_2]$	219	221	219
12	$[C_2C_1im][SAc]$	188	190	187
13	$[C_2C_1C_1im]Br$	299	299	300
14	$[C_2C_1C_1im][OAc]$	221	222	219

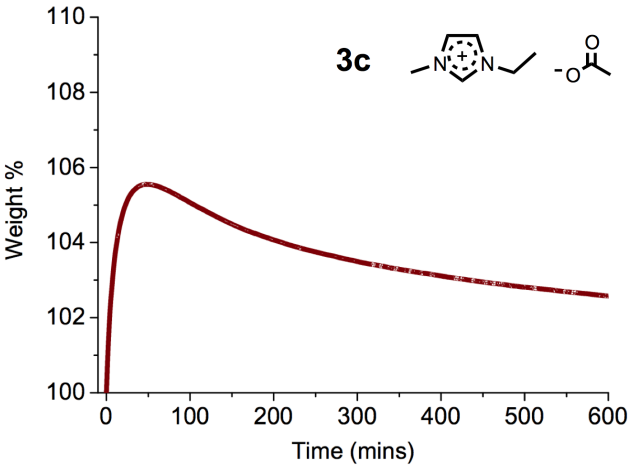


Fig. E2: Gain and loss of weight of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$ **3c**, during the 10-hour 80 ^{o}C drying procedure incorporating a CO_2 carrier gas.

Isothermal TGA experiments were conducted for 1-ethyl-3-methylimidazolium acetate, **3a**, and 1-ethyl-2,3-dimethylimidazolium acetate, **14**. Between 6 - 8 mg of **3a** / **14** was measured into the platinum pan. A **longer drying period** of 2 hours at 90 °C was employed.** The sample was then heated rapidly to the experiment temperature and maintained at this temperature for a period of 2 - 10 hours. All TGA data was processed in Microsoft Excel. Graphs were prepared using the Origin Pro v. 8.5 package.

* *The drying procedure was justified since the onset decomposition temperature of each compound is substantially higher (> 90 °C) than the 80 °C drying temperature, and the drying period is short. Therefore, actual decomposition of each ionic liquid during the drying period will be negligible.*

** *This drying period was justified based on several observations: (i) The T_{onset} temperatures of **3a** and **14** were found to be > 210 °C, significantly higher than the drying temperature; (ii) Ionic liquids **3a** and **14** were held at 90 °C for 72 hours during a test experiment. For each ionic liquid, a sharp loss of weight was observed in the first two hours, assigned to loss of water, followed by extremely slow weight loss in the remaining 70 hours (< 0.035% per hour). (iii) The ^{1}H NMR spectra of **3a** and **14** were unchanged following the 72-hour test experiments (Fig. 1). Therefore, decomposition of each ionic liquid during the two-hour drying period is negligible.*

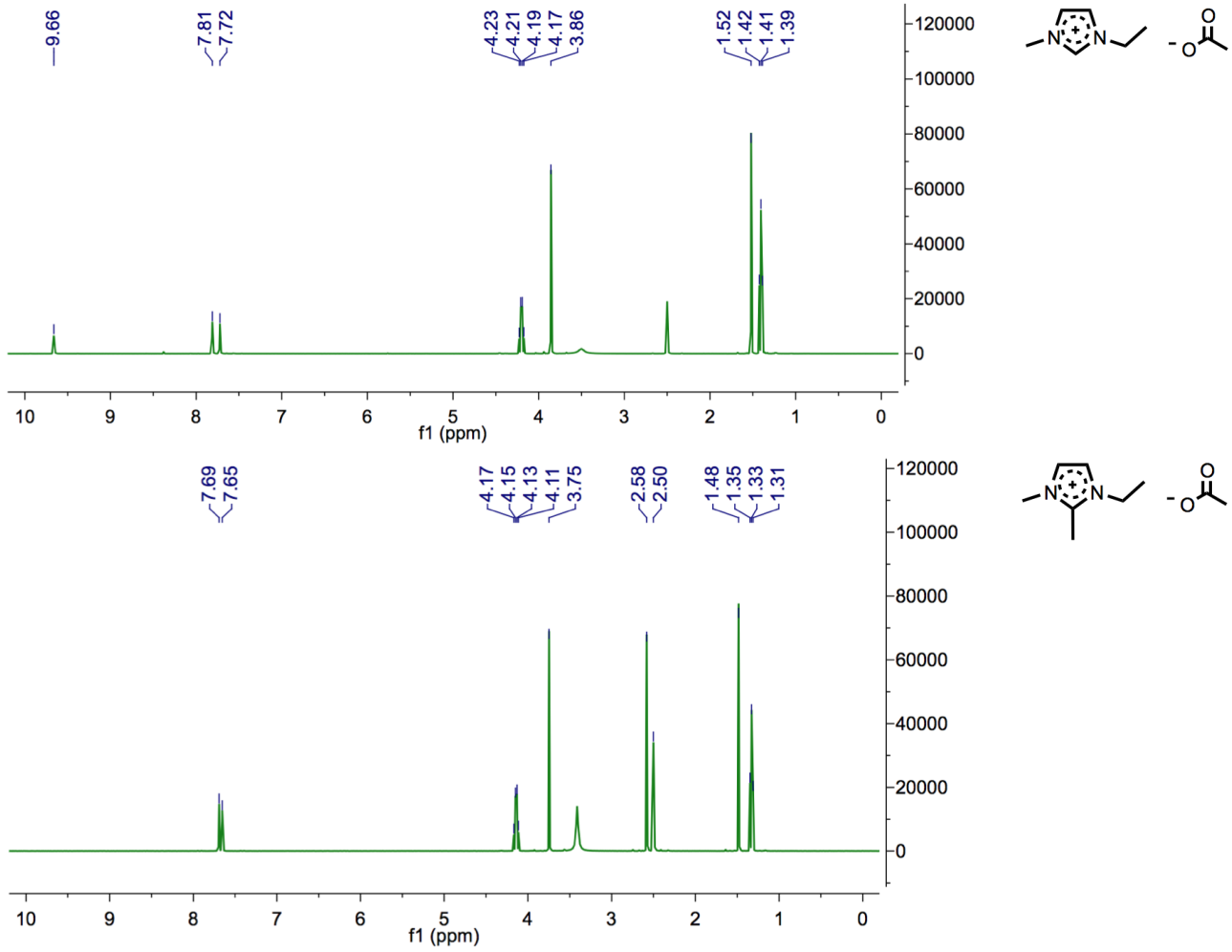


Fig E3: ^{1}H NMR spectra of [C_2C_1im][OAc], **3a** (top), and [$C_2C_1C_1$im][OAc], **14** (bottom), following the 72 h / 90 °C drying experiments.

The $T_{0.01/10}$ values for [C_2C_1im][OAc], **3a,** and [$C_2C_1C_1$im][OAc], **14** were determined using the method of MacFarlane and co-workers:[3]

(i) Linear decomposition 'curves' are collected at varying temperatures, and the gradients are determined.
(ii) The $t_{0.99}$ value (time taken for 1% weight loss to occur) is extracted from the gradient of the isotherm.
(iii) A plot of $t_{0.99}$ vs. temperature gives an exponential relationship, which can be extrapolated or interpolated to give the temperature corresponding to $t_{0.99}$ = 10 hours / 600 mins.

$T_{0.01/10}$ was determined as 102 °C for [C_2C_1im][OAc], **3a**, and 99 °C for [$C_2C_1C_1$im][OAc], **14**.

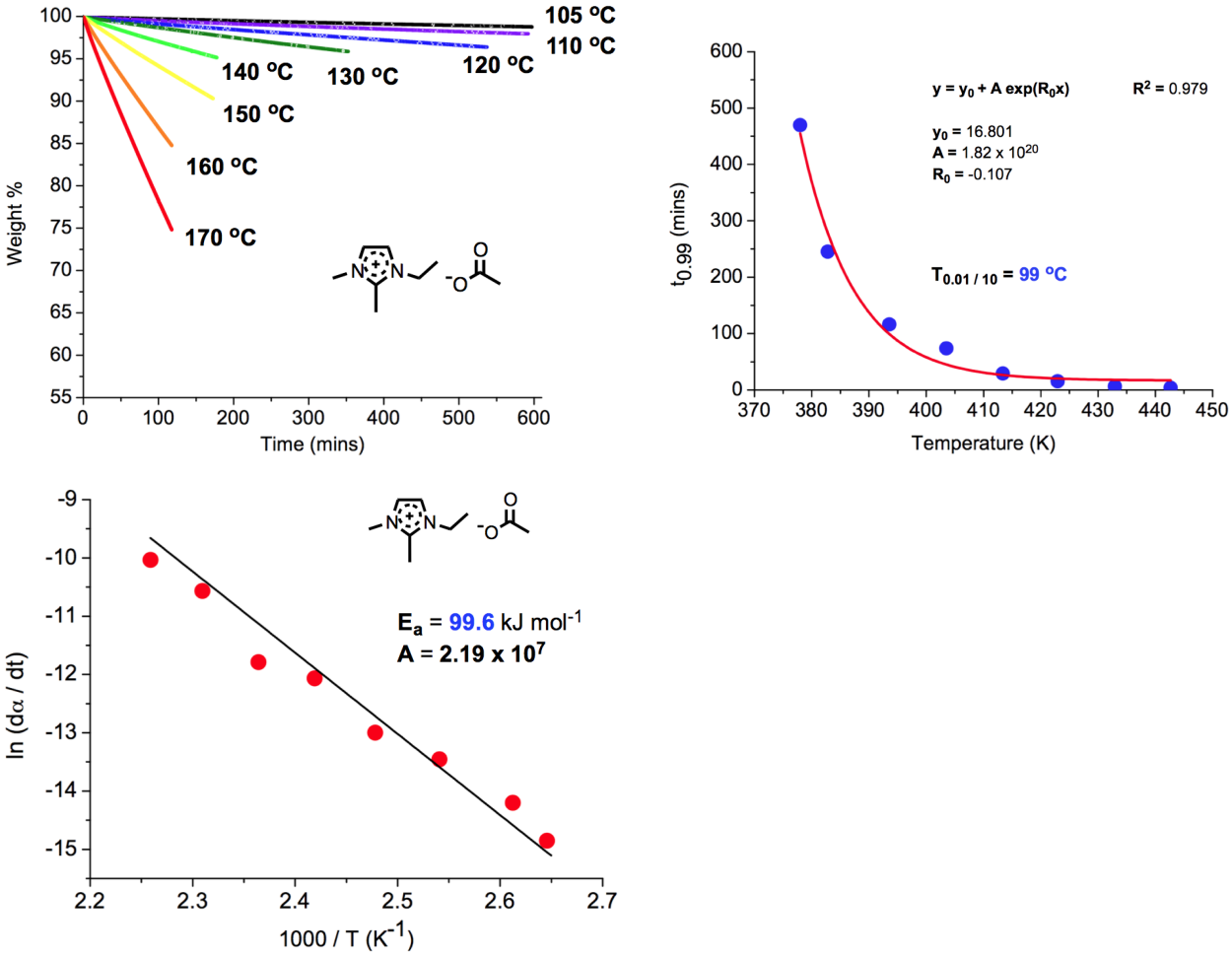


Fig E4: Isothermal TGA and $T_{0.01/10}$ determination for [$C_2C_1C_1$im][OAc], **14**.

4. Thermogravimetric Analysis - Mass Spectrometry (TGA-MS) Procedures

Thermogravimetric Analysis - Mass Spectrometry (TGA-MS) data was obtained on a PerkinElmer 'Pyris 1 TGA' Thermogravimetric Analyzer, using ceramic pans. Between 20 - 60 mg of the ionic liquid was measured into the ceramic pan. A heating rate of 10 ^{o}C min^{-1} and a CP Grade helium flow of 20 ml min^{-1} were used. The TGA was connected to a 'Hiden Analytical HPR 20' Mass Spectrometer with a ceramic heated capillary. Electron Ionisation (EI) mass spectrometry was employed, with an ionisation energy of 70 eV. All TGA-MS data was processed in Microsoft Excel. Graphs were prepared using the Origin Pro v. 8.5 package.

TGA-MS data is shown below for [C_2C_1im][NTf_2], **2**, [C_2C_1im][$CH_3(CH_2)_6CO_2$], **8** and [$C_2C_1C_1$im][OAc], **14**.

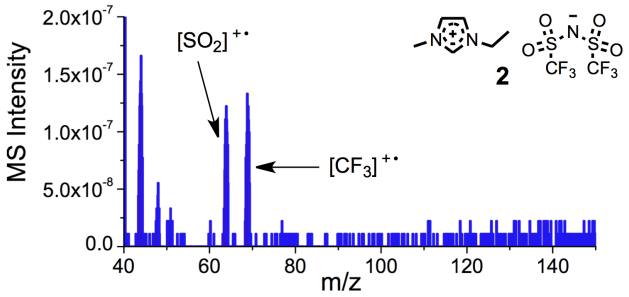


Fig E5: MS Histogram taken during the main decomposition period of [C_2C_1im][NTf_2], **2**, in the TGA-MS experiment.

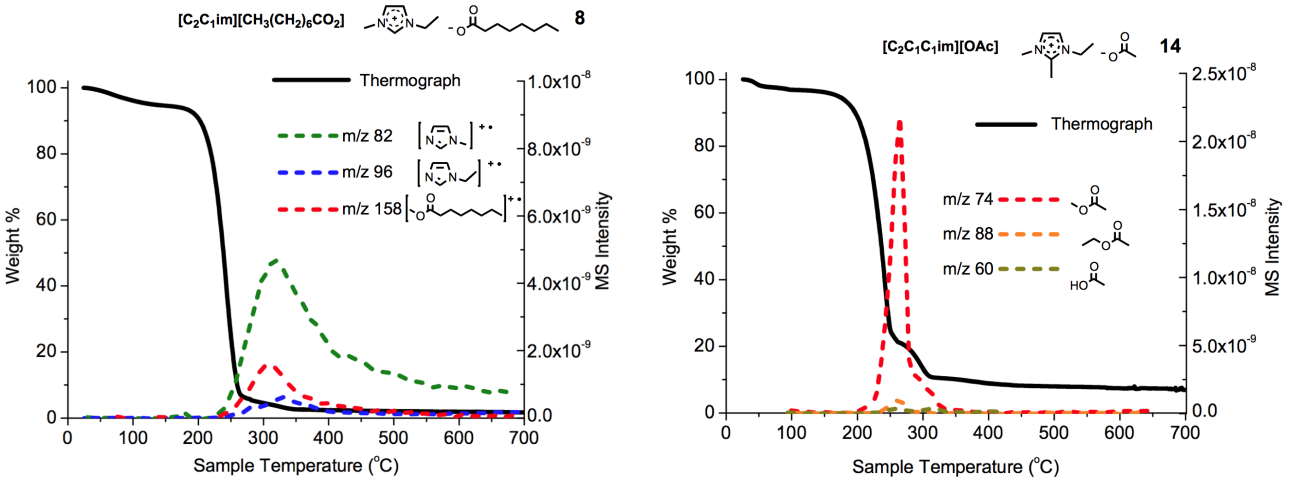


Fig E6: TGA-MS data for [C_2C_1im][$CH_3(CH_2)_6CO_2$], **8** and [$C_2C_1C_1$im][OAc], **14**. The solid black lines represent the TGA thermographs, the coloured dotted lines represent the intensities of certain m/z values as a function of temperature. The m/z values are assigned to parent peaks of small-molecule thermal decomposition products.

5. Differential Scanning Calorimetry (DSC) Procedures

Differential Scanning Calorimetry (DSC) results were obtained on a PerkinElmer 'Diamond DSC' Differential Scanning Calorimeter, fitted with a PerkinElmer 'Intracooler 2P' cooling accessory. Aluminium sample pans of diameter 7 mm were used. Between 1 - 9 mg of the ionic liquid was measured into the aluminium sample pan. A small incision was made in the tops of both the sample and reference pans. A **drying procedure** was then implemented: the sample pan was heated to 100 ^{o}C for 30 minutes in the calorimeter, to remove water. The sample pan was then quickly re-weighed, in order to determine the dry weight of the ionic liquid. The sample pan and reference pan were then replaced into the calorimeter, and the experiment was initiated:

- Isothermal at 30 ^{o}C for 1 minute
- Heat from 30 ^{o}C to 410 ^{o}C at a rate of 2.5 ^{o}C min^{-1}.
- Cool from 410 ^{o}C to 30 ^{o}C at a rate of 20 ^{o}C min^{-1}.
- Isothermal at 30 ^{o}C for 15 minutes.
- Heat from 30 ^{o}C to 410 ^{o}C at a rate of 2.5 ^{o}C min^{-1}.

DSC results for $[C_2C_1im][CF_3CO_2]$, **4**, $[C_2C_1im][c\text{-}(C_3H_5)CO_2]$, **11** and $[C_2C_1C_1im][OAc]$, **14**, are shown below, with temperature-ramped TGA thermographs overlaid:

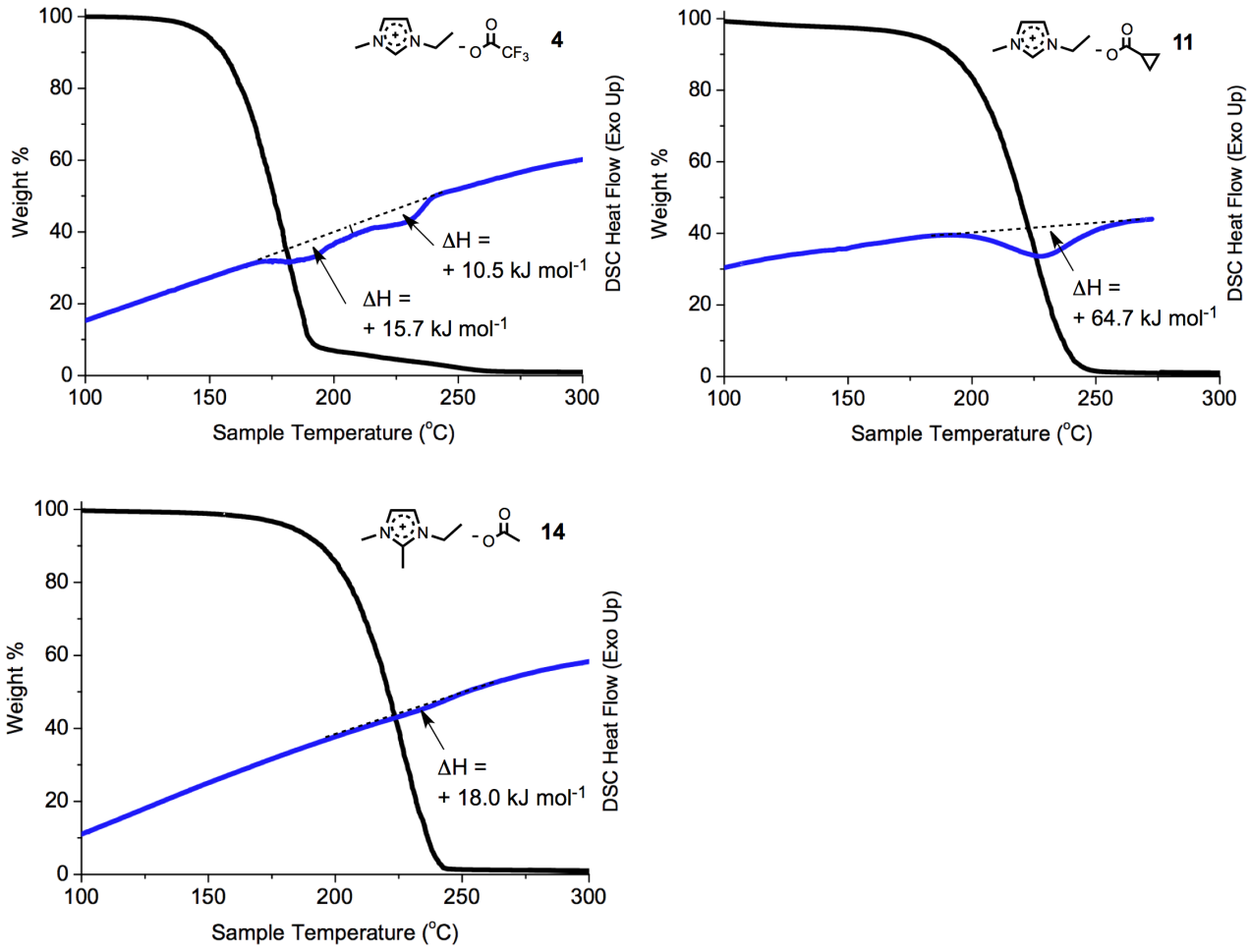


Fig E7: DSC graphs representing the thermal decomposition of $[C_2C_1im][CF_3CO_2]$, **4**, $[C_2C_1im][c\text{-}(C_3H_5)CO_2]$, **11** and $[C_2C_1C_1im][OAc]$, **14**. The DSC traces are overlaid with a TGA thermograph. DSC and TGA data were collected with a heating rate of 2.5 ^{o}C min^{-1}.

6. Computational Methods

DFT calculations were performed using the GAUSSIAN 09 suite of programs.[4] The B3LYP (Becke's three-parameter exchange[5] in combination with the Lee, Yang, Parr correlation[6]) functional, including the Grimme empirical dispersion correction (D2)[7], here on referred to as B3LYP-D, was employed for all calculations together with the 6-311++G(d,p) basis set. The inclusion of dispersion forces has been shown to be necessary when investigating ionic liquid systems.[8] The Basis Set Superposition Errors (BSSE) were determined using the counterpoise method for all ion pair conformers, and were found to be small (< 5 kJ mol^{-1}).[9] Convergence criteria were tightened above the default Gaussian values to 10^{-9} on the RMS density matrix and 10^{-7} on the energy. In addition, the numerical integration grid was enhanced from the default, with an optimised grid of 99 radial shells and 590 angular points per shell. The tighter convergence criteria were employed for optimisation calculations and single-point calculations (e.g. frequency calculations, counterpoise corrections).

All optimised structures were confirmed as minima or transition states by frequency analysis. All calculations were performed under no symmetry constraints. For the majority of structures, a three-stage optimisation process was employed: (i) initially optimisation was performed using the B3LYP functional and the smaller 6-31G(d) basis set; (ii) secondly, optimisation was continued using the B3LYP functional and the larger 6-311++G(d,p) basis set; (iii) finally, the dispersion corrected B3LYP-D functional was employed using the 6-311++G(d,p) basis set.

The Intrinsic Reaction Coordinate (IRC) protocol was employed to confirm that all transition state structures linked the assigned starting materials and products.[10] Population analysis was undertaken using the Natural Bond Orbital (NBO) method (version 5.9).[11] The NBO method was chosen because it is known to be less sensitive to the basis set, compared, for example, to Mulliken population analysis.[12]

7. Ion Pair and Transition State Energies

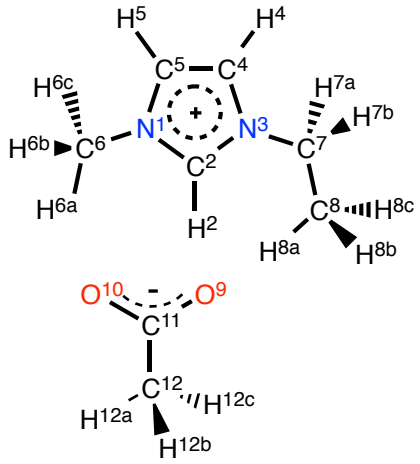
Ion pair geometries were located for 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, and 1-ethyl-2,3-dimethylimidazolium acetate, $[C_2C_1C_1im][OAc]$. Initially, the imidazolium-type cation and acetate anion were optimised separately. Subsequently, the acetate anion was positioned around the cation in chemically intuitive positions, and the ion pair conformer was optimised. Energies of the ion pair conformers (Tables E2 and E3), and the NBO charges for the lowest energy conformer (Figs. E8 and E9), are displayed below for each ionic liquid.

Table E2: Ion pair energies for 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$.

Ion Pair $[C_2C_1im][OAc]$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})	ΔZPE (kJ mol^{-1})	$BSSE$ (kJ mol^{-1})	$\Delta E_{ZPE+BSSE}$ (kJ mol^{-1})
Front Methyl + Ethyl	0.0	0.0	0.0	0.0	3.2	0.0
Front Ethyl	3.2	6.0	2.7	-0.9	3.0	4.9
Front Methyl	3.5	5.8	2.3	-0.7	2.8	4.9
Top	11.0	9.1	-1.9	2.3	3.8	9.4
Side Ethyl (Down)	42.0	41.6	-0.4	0.7	3.5	41.4
Side Methyl	43.8	46.4	2.6	0.2	3.1	46.0
Side Ethyl (Up)	46.9	44.8	-2.1	2.2	3.5	44.9
Back Methyl	57.2	61.5	4.3	-1.5	2.5	59.6
Back Ethyl	57.3	56.6	-0.7	0.3	2.7	55.7

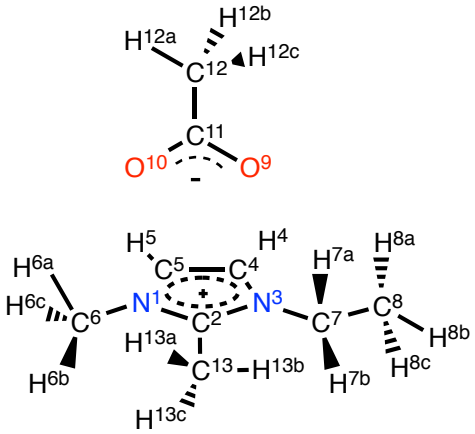
Table E3: Ion pair energies for 1-ethyl-2,3-dimethylimidazolium acetate, $[C_2C_1C_1im][OAc]$.

Ion Pair $[C_2C_1C_1im][OAc]$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})	ΔZPE (kJ mol^{-1})	$BSSE$ (kJ mol^{-1})	$\Delta E_{ZPE+BSSE}$ (kJ mol^{-1})
Top Methyl 1	0.0	0.0	0.0	0.0	4.4	0.0
Top Methyl 2	0.3	-2.6	-2.9	0.6	4.7	-1.8
Bottom	1.0	-0.9	-1.9	0.3	4.4	-0.6
Top Ethyl	5.8	-3.9	-9.8	1.2	4.5	-1.0
Side Ethyl	24.9	31.9	7.0	-2.3	3.5	29.9
Side Methyl	34.1	32.7	-1.4	-2.6	3.2	33.2
Back Ethyl	41.9	49.3	7.4	-2.7	2.7	46.4
Back Methyl	43.1	52.2	9.1	-4.2	2.5	48.7



Atom	Charge	Atom	Charge	Atom	Charge
N^1	-0.36	C^6	-0.38	O^9	-0.82
N^3	-0.38	H^{6a}	0.30	O^{10}	-0.78
C^2	0.29	H^{6b}	0.20	C^{11}	0.80
H^2	0.31	H^{6c}	0.20	C^{12}	-0.67
C^4	-0.03	C^7	-0.16	H^{12a}	0.20
H^4	0.22	H^{7a}	0.21	H^{12b}	0.21
C^5	-0.03	H^{7b}	0.19	H^{12c}	0.21
H^5	0.23	C^8	-0.60		
		H^{8a}	0.26		
		H^{8b}	0.20		
		H^{8c}	0.21		

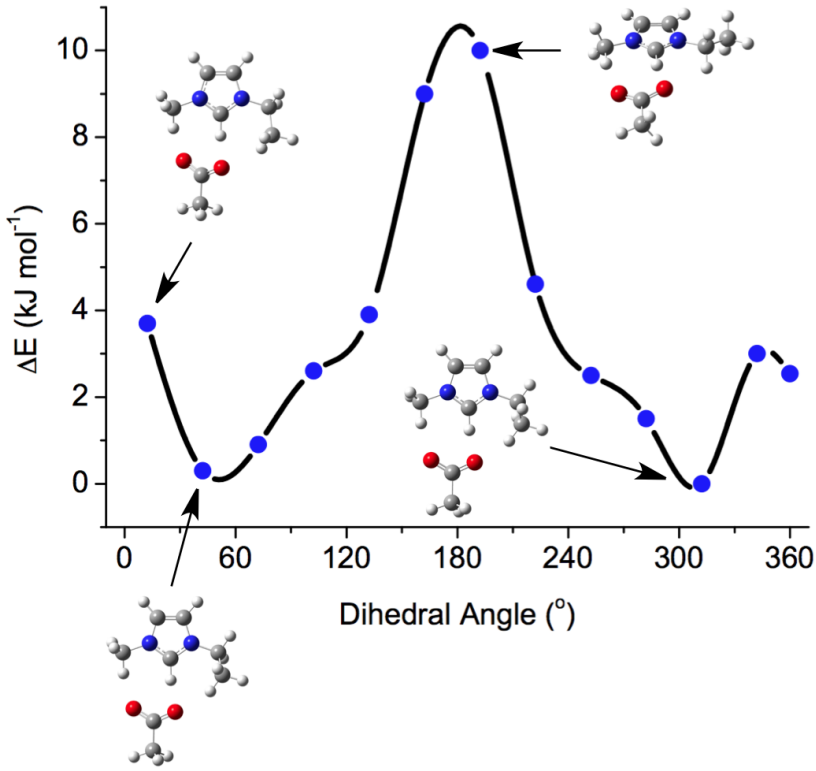
Fig E8: Atomic numbering scheme and NBO charges for the lowest energy 'Front Methyl + Ethyl' ion pair conformer of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$.



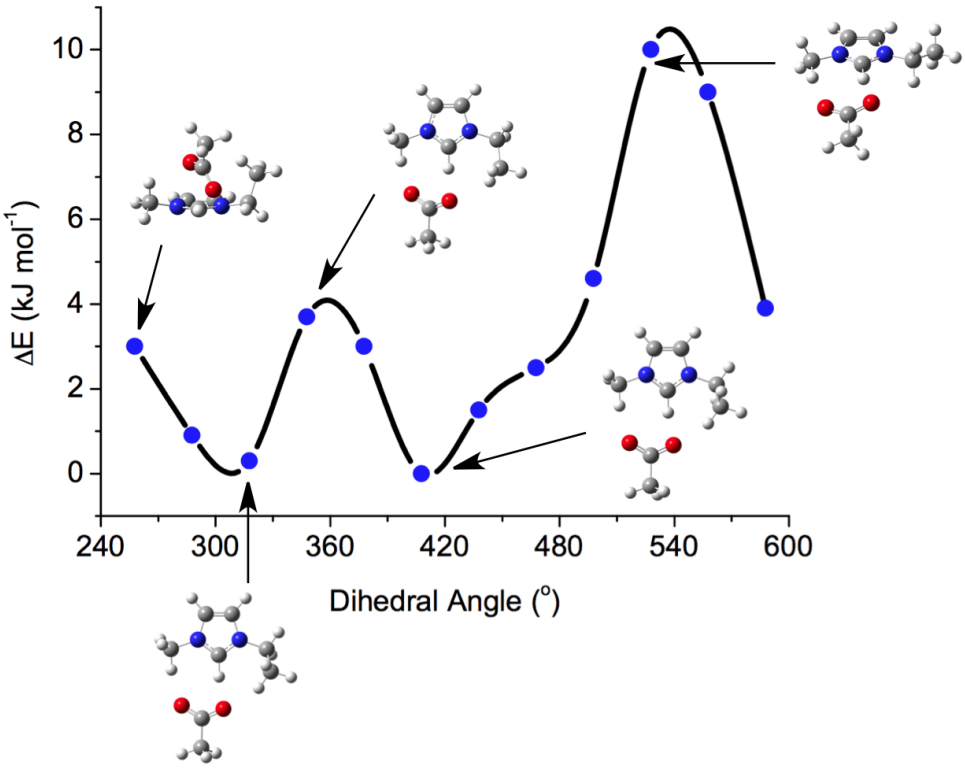
Atom	Charge	Atom	Charge	Atom	Charge
N^1	-0.37	C^6	-0.38	O^9	-0.82
N^3	-0.37	H^{6a}	0.29	O^{10}	-0.81
C^2	0.56	H^{6b}	0.20	C^{11}	0.78
C^{13}	-0.65	H^{6c}	0.20	C^{12}	-0.68
H^{13a}	0.29	C^7	-0.18	H^{12a}	0.20
H^{13b}	0.24	H^{7a}	0.26	H^{12b}	0.20
H^{13c}	0.21	H^{7b}	0.19	H^{12c}	0.21
C^4	-0.03	C^8	-0.59		
H^4	0.23	H^{8a}	0.21		
C^5	-0.03	H^{8b}	0.22		
H^5	0.22	H^{8c}	0.20		

Fig E9: Atomic numbering scheme and NBO charges for the lowest energy 'Top Methyl 1' ion pair conformer of 1-ethyl-2,3-dimethylimidazolium acetate, $[C_2C_1C_1im][OAc]$.

Conformational analysis of the ethyl side chain was performed for two low energy ion pair conformers of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, the 'Front Methyl + Ethyl' and 'Top' conformers. The C^2-N-C_α-C_β dihedral angle was increased in increments of 30°, and the ion pair was optimised with no additional constraints. The results are displayed below (Fig. E10).



(a)



(b)

Fig E10: Change in energy and structure of the (a) 'Front Ethyl + Methyl' and (b) 'Top' ion pair conformers of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, upon rotation of the C^2-N-C_α-C_β dihedral angle (ethyl side-chain). Energies are uncorrected.

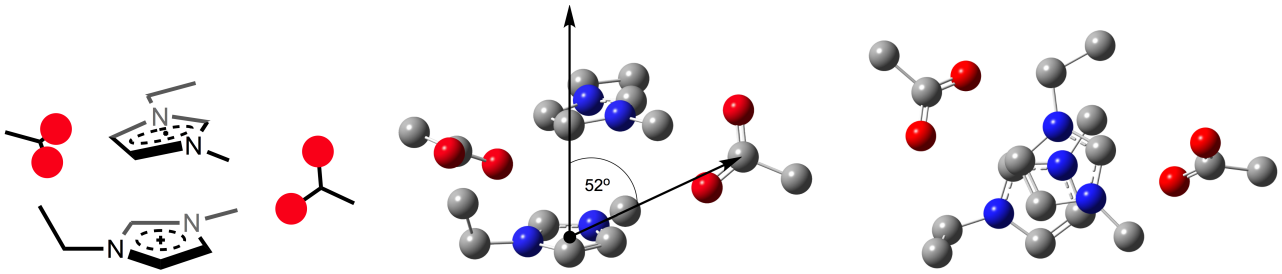


Fig E11: Diagrams representing a low-energy dimer structure for $[C_2C_1im][OAc]$, demonstrating the angle between an imidazolium ring normal vector and the line between the centre of the ring and an acetate carboxylate carbon atom. The acetate anion sits roughly midway between the two π-stacked rings, explaining the large out-of plane angle. Hydrogen atoms are omitted for clarity.

The thermal decomposition mechanisms investigated in this study are shown in Figure E12. The energies of transition state and product structures for 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$ (mechanisms B1-D1) and 1-ethyl-2,3-dimethylimidazolium acetate, $[C_2C_1C_1im][OAc]$ (mechanisms A2-D2) are displayed below (Tables E4 and E6). The decomposition reaction profiles and transition state structure for mechanism A2 is displayed in Figure E13.

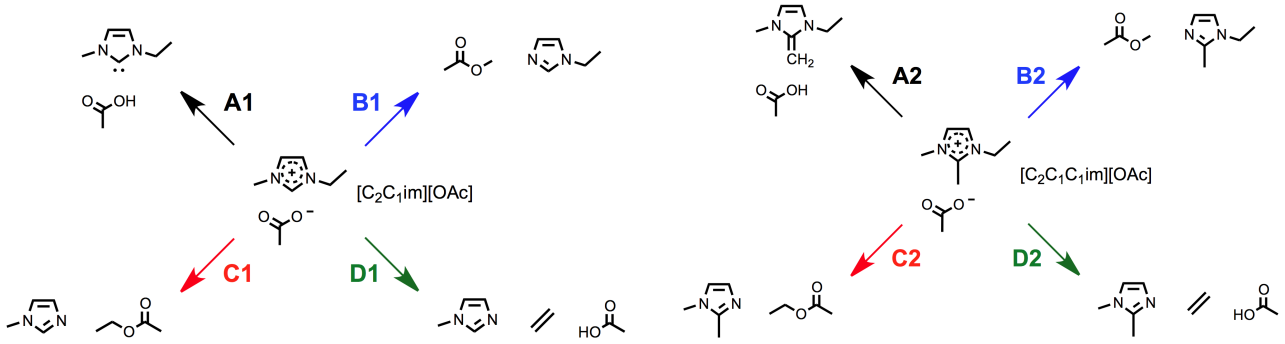


Fig E12: Decomposition routes A1-D1 and A2-D2 for 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, 1-ethyl-2,3-dimethylimidazolium acetate, $[C_2C_1C_1im][OAc]$, respectively.

Table E4: Transition state energies and product energies for decomposition mechanisms of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, and 1-ethyl-2,3-dimethylimidazolium acetate, $[C_2C_1C_1im][OAc]$, relative to the lowest energy ion pair of each ionic liquid.

Mechanism	**Ion Pair** (kJ mol^{-1})					**TS** (kJ mol^{-1})					**Product** (kJ mol^{-1})				
	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}
B1	0.0	0.0	0.0	0.0	0.0	134.6	139.5	4.9	-4.3	139.1	-35.3	0.6	35.9	-2.8	4.0
C1	0.0	0.0	0.0	0.0	0.0	135.4	136.2	0.8	-3.9	135.6	-39.6	-3.0	36.7	-3.5	0.2
D1	0.0	0.0	0.0	0.0	0.0	156.1	156.8	0.7	-16.8	156.4	-25.8	63.3	89.1	-16.6	61.3
B2	0.0	0.0	0.0	0.0	0.0	118.5	119.1	0.5	0.0	119.8	-41.1	-1.0	40.1	-0.2	2.3
C2	0.0	0.0	0.0	0.0	0.0	119.3	114.8	-4.6	0.0	116.7	-41.7	-5.2	36.5	-0.1	-0.1
D2	0.0	0.0	0.0	0.0	0.0	137.7	138.6	0.9	0.0	138.6	-27.8	61.1	88.9	-0.2	61.0

Table E5: ΔE_{ZPE}, ν, $\Delta E_{ZPE} + \nu$ ('ΔE_{eff}') and ΔE_{SCF} energies for the ion pair, transition state (TS) and Carbene-Acid Pair (CAP) structures relating to mechanism A1 of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$.
[a] = C^2-H stretch; [b] = TS vibrational mode; [c] = O-H stretch.

Structure	ΔE_{ZPE} (kJ mol^{-1})	ν (cm^{-1})	ν (kJ mol^{-1})	$\Delta E_{ZPE} + \nu$ (kJ mol^{-1})	normalised $\Delta E_{ZPE} + \nu$ (kJ mol^{-1})	ΔE_{SCF} (kJ mol^{-1})
Ion Pair	0.0	2506.63 [a]	-30.0	-30.0	0.0	0.0
TS	1.7	727.62 [b]	(-8.7)	1.7	31.7	12.6
CAP	11.5	2139.19 [c]	-25.6	-14.1	15.9	13.7

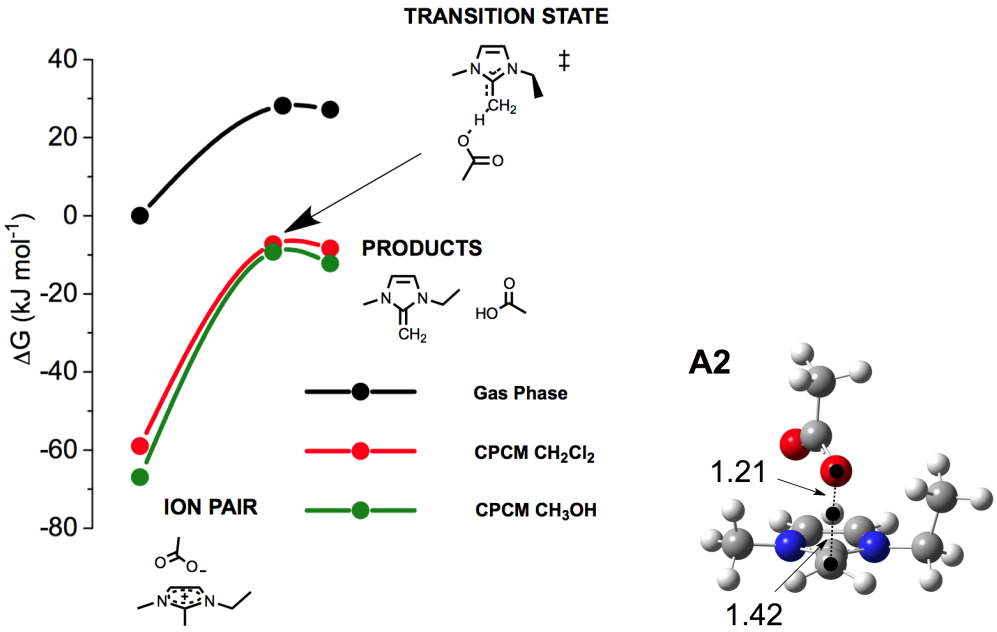


Fig. E13: Decomposition of $[C_2C_1C_1im][OAc]$ at the C^2 position (mechanism A2), in the gas phase and using the CPCM environment, and gas phase transition state structure. Bond distances are in angstroms.

Table E6: Transition state energies and product energies for decomposition mechanism **A2** of 1-ethyl-2,3-dimethylimidazolium acetate, $[C_2C_1C_1im][OAc]$, relative to the lowest energy ion pair.

Mechanism **A2**	**Ion Pair** (kJ mol^{-1})					**TS** (kJ mol^{-1})					**Product** (kJ mol^{-1})				
	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}	ΔG	ΔH	$T\Delta S$	ΔZPE	ΔE_{ZPE}
Gas Phase	0.0	0.0	0.0	0.0	0.0	28.1	22.0	-6.1	0.0	24.1	27.2	72.5	45.3	0.0	73.1
CPCM CH_2Cl_2	0.0	0.0	0.0	0.0	0.0	51.7	45.3	-6.3	0.0	47.6	50.6	93.5	42.9	0.0	94.6
CPCM MeOH	0.0	0.0	0.0	0.0	0.0	57.7	51.9	-5.8	0.0	54.4	54.8	98.4	43.7	0.0	99.6

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