# Electronic supporting information for

"The effect of an ionic liquid on the rate of reaction at a phosphorus centre"

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## Table of Contents

## Representative NMR spectra demonstrating the extent of byproduct formation

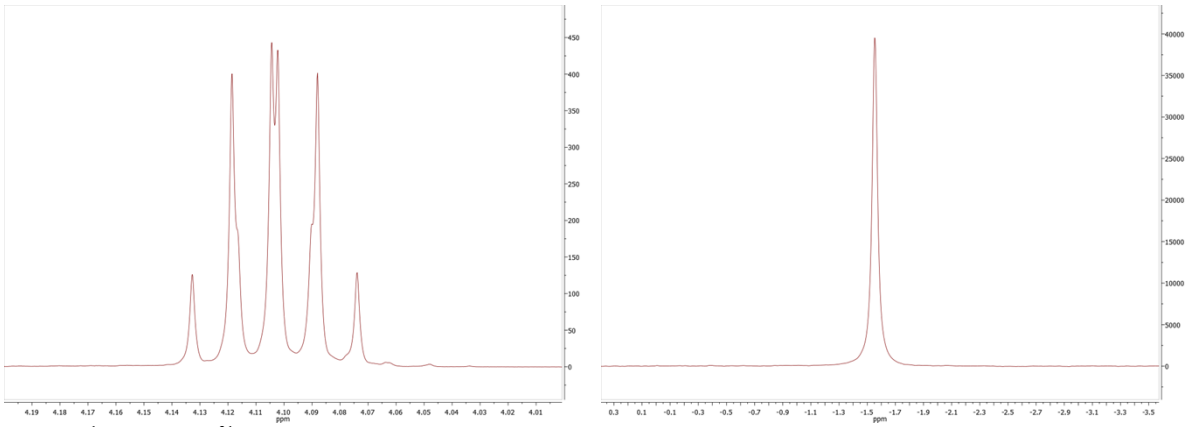

**Fig. S1** $^{1}$H (left) and $^{31}$P (right) NMR spectra (500 and 202 Hz, respectively) for the reaction of diethyl chlorophosphate in ethanol. In the $^{1}$H NMR spectrum the signal at $\delta$ *ca.* 4.1 corresponds to the triester (triethyl phosphate) and the signal at $\delta$ *ca.* 4.06 corresponds to the diester (diethyl hydrogen phosphate, confirmed through spiking experiments); here the latter is *ca.* 1% of the product mixture. In the $^{31}$P NMR spectrum, no signal due to the diester could be seen (the signal shown is due to the triester). Spiking experiments demonstrated that the signal due to the diester is masked entirely here by the signal due to the triester.

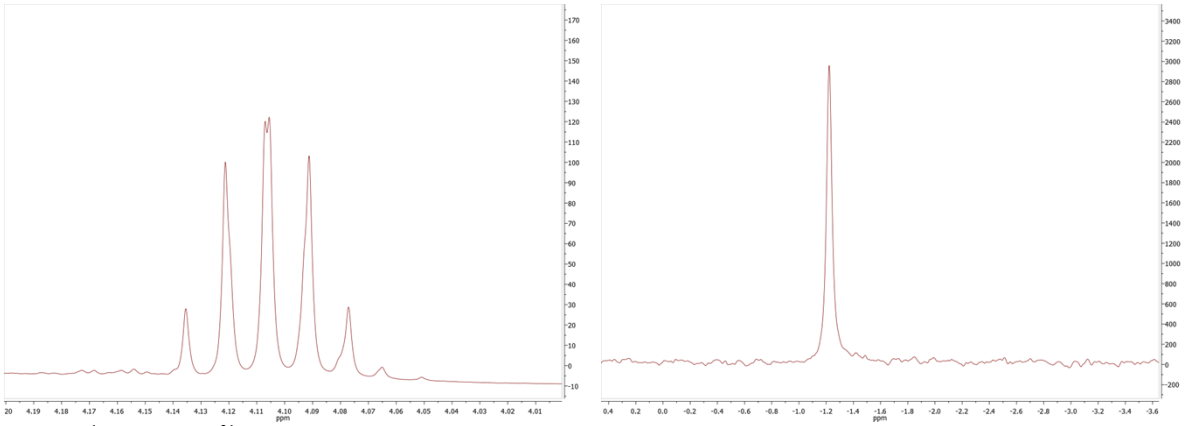

**Fig. S2** $^{1}$H (left) and $^{31}$P (right) NMR spectra (500 and 202 MHz, respectively) for the reaction of diethyl chlorophosphate with ethanol in acetonitrile. In the $^{1}$H NMR spectrum the signal at $\delta$ *ca.* 4.1 corresponds to the triester (triethyl phosphate) and the signal at $\delta$ *ca.* 4.06 corresponds to the diester (diethyl hydrogen phosphate, confirmed through spiking experiments); here the latter is *ca.* 1% of the product mixture. In the $^{31}$P NMR spectrum, no signal due to the diester could be seen (the signal shown is due to the triester). Spiking experiments demonstrated that the signal due to the diester is masked entirely here by the signal due to the triester.

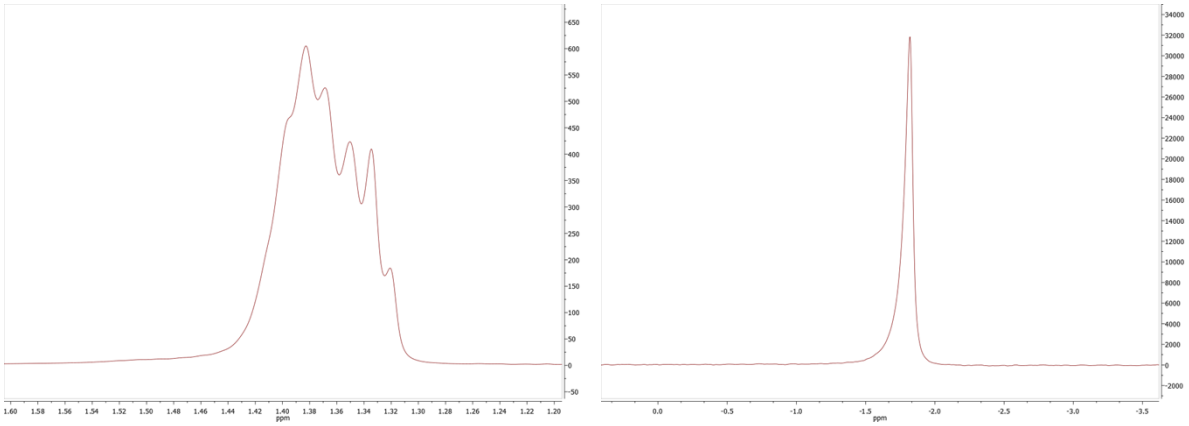

**Fig. S3** $^{1}$H (left) and $^{31}$P (right) NMR spectra (500 and 202 MHz, respectively) for the reaction of diethyl chlorophosphate with ethanol in [bmim][$(CF_3SO_2)_2N$] at $\chi_{IL}$ 0.31. In the $^{1}$H NMR spectrum, the signal due to the diester diethyl hydrogen phosphate appears at $\delta$ *ca.* 1.3 (confirmed through spiking experiments); none is observable here.[a] In the $^{31}$P NMR spectrum, no signal due to the diester could be seen (the signal shown is due to the triester, triethyl phosphate). Spiking experiments demonstrated that the signal due to the diester is masked entirely here by the signal due to the triester.

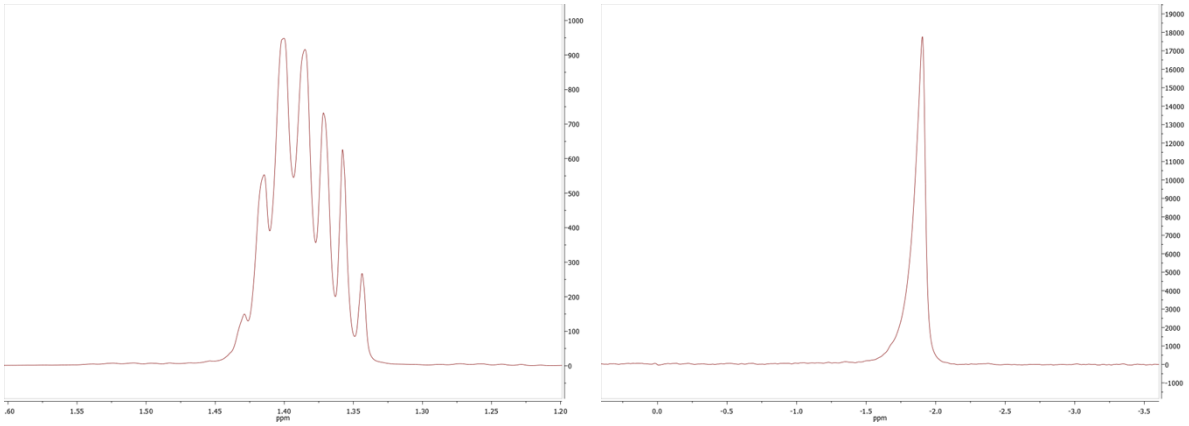

**Fig. S4** $^{1}$H (left) and $^{31}$P (right) NMR spectra (500 and 202 MHz, respectively) for the reaction of diethyl chlorophosphate with ethanol in [bmim][$(CF_3SO_2)_2N$] at $\chi_{IL}$ 0.60. In the $^{1}$H NMR spectrum, the signal due to the diester diethyl hydrogen phosphate appears at $\delta$ *ca.* 1.3 (confirmed through spiking experiments); none is observable here.[b] In the $^{31}$P NMR spectrum, no signal due to the diester could be seen (the signal shown is due to the triester, triethyl phosphate). Spiking experiments demonstrated that the signal due to the diester is masked entirely here by the signal due to the triester.

[a] This signal is used as the ionic liquid signals obscures those signals used in molecular solvents.
[b] This signal is used as the ionic liquid signals obscures those signals used in molecular solvents.

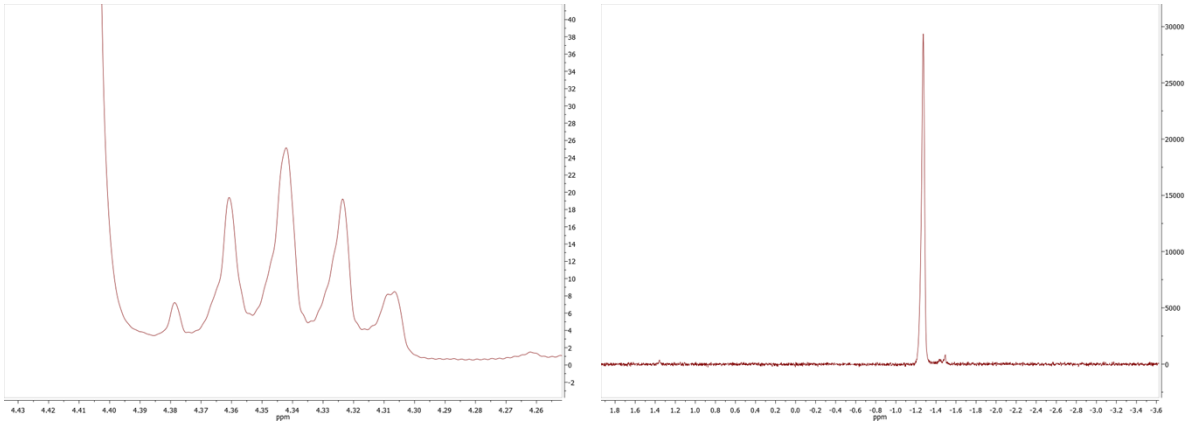

**Fig. S5** $^{1}$H (left) and $^{31}$P (right) NMR spectra (400 and 162 MHz, respectively) for the reaction of diethyl chlorophosphate with ethanol in [bmim][$(CF_3SO_2)_2N$] and acetonitrile at $\chi_{IL}$ 0.35. In the $^{1}$H NMR spectrum, the signal due to the diester diethyl hydrogen phosphate appears at $\delta$ *ca.* 4.3 (confirmed through spiking experiments) though detection is difficult. In the $^{31}$P NMR spectrum, the signal at $\delta$ *ca.* -1.2 corresponds to the triester (triethyl phosphate) and the signal at $\delta$ *ca.* -1.5 corresponds to the diester product (confirmed through spiking experiments); here the latter is *ca.* 1% of the product mixture.

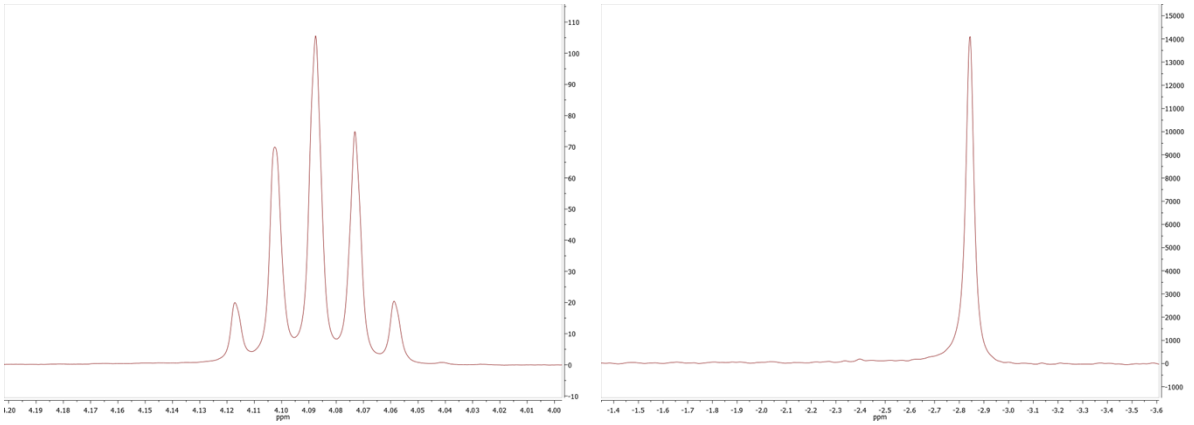

**Fig. S6** $^{1}$H (left) and $^{31}$P (right) NMR spectra (500 and 202 MHz, respectively) for the reaction of diethyl chlorophosphate with ethanol in ethanol containing lithium bis(trifluoromethylsulfonyl)imide at $\chi_{salt}$ 0.15. In the $^{1}$H NMR spectrum the signal at $\delta$ *ca.* 4.08 corresponds to the triester (triethyl phosphate) and the signal at $\delta$ *ca.* 4.04 corresponds to the diester (diethyl hydrogen phosphate, confirmed through spiking experiments); here the latter is < 1% of the product mixture. In the $^{31}$P NMR spectrum, the signal at $\delta$ *ca.* -2.8 corresponds to the triester product and the signal at $\delta$ *ca.* -2.4 corresponds to the diester product (confirmed through spiking experiments); quantification was not practical on this signal.

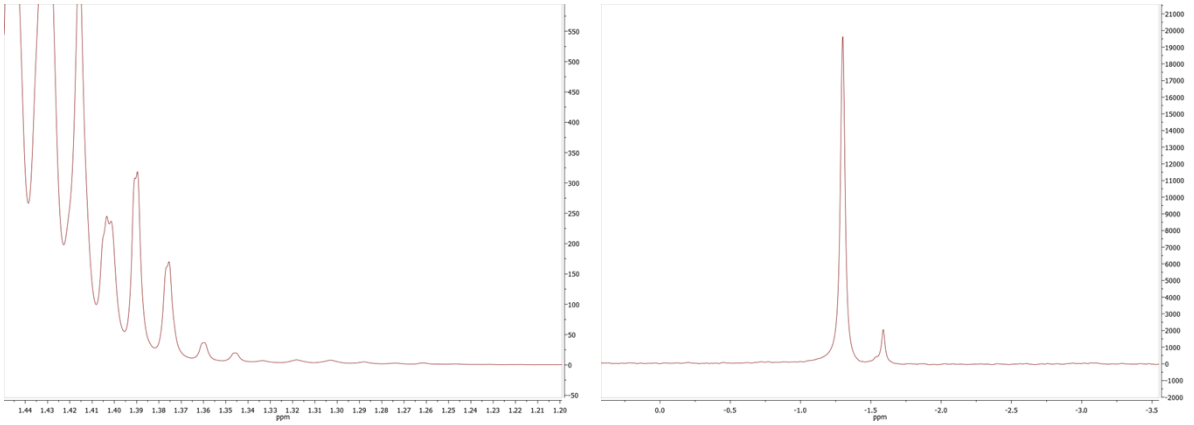

**Fig. S7** $^{1}$H (left) and $^{31}$P (right) NMR spectra (500 and 202 MHz, respectively) for the reaction of diethyl chlorophosphate with ethanol in ethanol containing [bmim][Cl] at $\chi_{salt}$ 0.15. In the $^{1}$H NMR spectrum, the signal due to the diester diethyl hydrogen phosphate appears at $\delta$ *ca.* 1.36 (confirmed through spiking experiments) and a significant proportion is detectable here, though it is difficult to quantify.[c] In the $^{31}$P NMR spectrum, the signal at $\delta$ *ca.* -1.2 corresponds to the triester (triethyl phosphate) and the signal at $\delta$ *ca.* -1.6 corresponds to the diester product (confirmed through spiking experiments); here the latter is *ca.* 8% of the product mixture

[c] This signal is used as the ionic liquid signals obscures those signals used in molecular solvents.

Rate data for the ethanolysis of diethyl chlorophosphate at different mole fractions of [bmim][$(CF_3SO_2)_2N$] in ethanol-$d_6$, shown in Fig. 1, main text:

**Table S1.** The rate constants for the ethanolysis of diethyl chlorophosphate at different mole fractions of [bmim][$(CF_3SO_2)_2N$] in ethanol-$d_6$ at 298.2 K. Uncertainties are the standard error of the mean derived from at least three replicate measurements at each mole fraction.

| Mole Fraction of ionic liquid | [ethanol-$d_6$] / mol $L^{-1}$ | $k_{obs}$ / $10^{-4}$ $s^{-1}$ | $k_2$ / $10^{-5}$ mol $L^{-1}$ $s^{-1}$ | Average $k_2$ / $10^{-5}$ mol $L^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| 0.00 | 16.4 | 1.14 | 0.70 | 0.75 ± 0.03 |
| | | 1.33 | 0.81 | |
| | | 1.24 | 0.75 | |
| 0.04 | 13.7 | 1.91 | 1.40 | 1.52 ± 0.07 |
| | | 2.08 | 1.52 | |
| | | 2.23 | 1.63 | |
| 0.12 | 9.59 | 2.18 | 2.27 | 2.15 ± 0.14 |
| | | 2.21 | 2.30 | |
| | | 1.80 | 1.88 | |
| 0.21 | 6.85 | 1.88 | 2.75 | 2.73 ± 0.04 |
| | | 1.90 | 2.78 | |
| | | 1.82 | 2.66 | |
| 0.31 | 4.93 | 1.48 | 3.00 | 3.00 ± 0.06 |
| | | 1.43 | 2.90 | |
| | | 1.53 | 3.11 | |
| 0.41 | 3.56 | 1.09 | 3.07 | 2.86 ± 0.12 |
| | | 1.01 | 2.84 | |
| | | 0.95 | 2.66 | |
| 0.48 | 2.74 | 0.62 | 2.28 | 3.09 ± 0.40 |
| | | 0.78 | 2.83 | |
| | | 1.14 | 4.17 | |
| | | 0.42 | 3.09 | |
| 0.61 | 1.64 | 0.26 | 1.59 | 2.30 ± 0.37 |
| | | 0.47 | 2.83 | |
| | | 0.41 | 2.48 | |
| 0.72 | 0.959 | -[a] | 1.22 | 1.38 ± 0.10 |
| | | -[a] | 1.34 | |
| | | -[a] | 1.57 | |

[a] At this concentration of ethanol-$d_6$, the reaction conditions are no longer pseudo-first order and the bimolecular rate constant ($k_2$) was calculated directly.

Rate data for the ethanolysis of diethyl chlorophosphate at different mole fractions of [bmim][$(CF_3SO_2)_2N$] in acetonitrile, shown in Fig 2, main text:

**Table S2.** The bimolecular rate constant ($k_2$) for the ethanolysis of diethyl chlorophosphate at different mole fractions of [bmim][$(CF_3SO_2)_2N$] in acetonitrile at 298.2 K with an ethanol-$d_6$ concentration of 0.959 mol $L^{-1}$. Uncertainties are the standard error of the mean derived from at least three replicate measurements at each mole fraction.

| Mole Fraction of ionic liquid | $k_2$ / $10^{-5}$ mol $L^{-1}$ $s^{-1}$ | Average $k_2$ / $10^{-5}$ mol $L^{-1}$ $s^{-1}$ |
|---|---|---|
| 0.00 | 0.119 | 0.14 ± 0.02 |
| | 0.140 | |
| | 0.153 | |
| 0.10 | 1.16 | 1.21 ± 0.10 |
| | 1.07 | |
| | 1.41 | |
| 0.21 | 2.05 | 1.83 ± 0.12 |
| | 1.65 | |
| | 1.80 | |
| 0.35 | 2.85 | 2.17 ± 0.37 |
| | 2.54 | |
| | 2.87 | |
| | 1.59 | |
| | 0.996 | |
| 0.41 | 1.90 | 1.89 ± 0.01 |
| | 1.89 | |
| | 1.87 | |
| 0.48 | 2121 | 2.09 ± 0.10 |
| | 1.90 | |
| | 2.17 | |
| 0.61 | 1.32 | 1.30 ± 0.05 |
| | 1.38 | |
| | 1.20 | |
| 0.72 | 1.22 | 1.38 ± 0.10 |
| | 1.34 | |
| | 1.57 | |

Rate data and Eyring plot for the ethanolysis of diethyl chlorophosphate used for the determination of the activation parameters, shown in Table 3, main text:

**Table S3** The rate constants for the ethanolysis of diethyl chlorophosphate at different mole fractions of [bmim][$(CF_3SO_2)_2N$] in ethanol-$d_6$ at various temperatures.

| Mole Fraction of ionic liquid | Temperature / K | [ethanol-$d_6$] / mol $L^{-1}$ | $k_{obs}$ / $10^{-4}$ $s^{-1}$ | $k_2$ / $10^{-5}$ mol $L^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| 0.00 | 277.7 | 16.4 | 0.161 | 0.0979 |
| | 277.7 | | 0.156 | 0.0948 |
| | 277.8 | | 0.136 | 0.0827 |
| | 285.7 | | 0.457 | 0.278 |
| | 285.8 | | 0.437 | 0.266 |
| | 285.9 | | 0.449 | 0.273 |
| | 297.5 | | 1.14 | 0.696 |
| | 297.9 | | 1.33 | 0.808 |
| | 298.0 | | 1.24 | 0.752 |
| | 314.1 | | 4.52 | 2.75 |
| | 314.1 | | 4.73 | 2.88 |
| | 314.2 | | 4.49 | 2.73 |
| 0.31 | 276.4 | 4.93 | 0.321 | 0.652 |
| | 276.7 | | 0.452 | 0.916 |
| | 276.7 | | 0.450 | 0.912 |
| | 286.1 | | 0.690 | 1.40 |
| | 286.1 | | 0.680 | 1.38 |
| | 286.1 | | 0.932 | 1.89 |
| | 297.9 | | 1.48 | 3.00 |
| | 297.9 | | 1.43 | 2.90 |
| | 297.9 | | 1.53 | 3.11 |
| | 297.9 | | 1.80 | 3.66 |
| | 307.0 | | 4.22 | 8.56 |
| | 307.0 | | 3.21 | 6.52 |
| | 307.0 | | 4.16 | 8.43 |
| | 320.5 | | 6.61 | 13.4 |
| | 320.8 | | 9.76 | 19.8 |
| | 320.8 | | 9.07 | 18.4 |
| 0.72 | 282.1 | 0.959 | -[a] | 0.390 |
| | 282.2 | | -[a] | 0.923 |
| | 282.2 | | -[a] | 0.597 |
| | 297.9 | | -[a] | 1.22 |
| | 297.9 | | -[a] | 1.34 |
| | 298.0 | | -[a] | 1.57 |
| | 313.8 | | -[a] | 5.24 |
| | 313.9 | | -[a] | 5.17 |
| | 313.9 | | -[a] | 5.46 |
| | 333.8 | | -[a] | 10.0 |
| | 333.8 | | -[a] | 16.9 |
| | 333.9 | | -[a] | 15.5 |

[a] At this concentration of ethanol-$d_6$, the reaction conditions are no longer pseudo-first order and the bimolecular rate constant ($k_2$) was calculated directly.

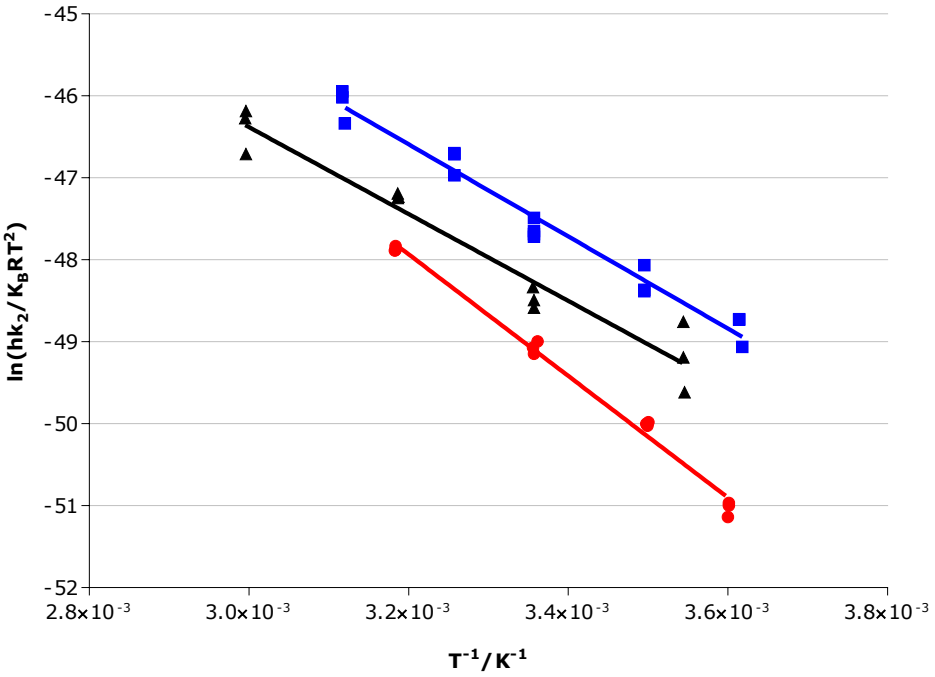


**Fig. S1.** Eyring plot from which the activation parameters were determined for the ethanolysis of diethyl chlorophosphate in ethanol-$d_6$ at the mole fractions of [bmim][$(CF_3SO_2)_2N$], 0 (**red**), 0.3 (**blue**) and 0.7 (**black**).

Rate data, Eyring plot and activation parameters for the ethanolysis of diethyl chlorophosphate in acetonitrile (not shown in main text):

**Table S4.** The rate constants for the ethanolysis of diethyl chlorophosphate at different mole fractions of [bmim][$(CF_3SO_2)_2N$] in acetonitrile with an ethanol-$d_6$ concentration of 0.959 mol $L^{-1}$ at various temperatures.

| Mole Fraction of ionic liquid | Temperature / K | $k_2$ / $10^{-5}$ mol $L^{-1}$ $s^{-1}$ |
|---|---|---|
| 0.00 | 298.1 | 0.158 |
| | 298.2 | 0.306 |
| | 298.4 | 0.299 |
| | 308.7 | 0.408 |
| | 308.8 | 0.325 |
| | 308.8 | 0.271 |
| | 320.4 | 0.598 |
| | 320.5 | 1.54 |
| | 329.0 | 3.06 |
| 0.35 | 287.5 | 0.889 |
| | 287.9 | 0.661 |
| | 298.2 | 0.996 |
| | 298.2 | 1.59 |
| | 298.2 | 2.85 |
| | 298.2 | 2.87 |
| | 298.2 | 2.54 |
| | 319.7 | 6.02 |
| | 320.2 | 4.01 |
| | 328.4 | 8.14 |
| | 328.4 | 8.22 |
| | 328.4 | 10.3 |
| | 328.5 | 23.8 |
| 0.72 | 282.1 | 0.390 |
| | 282.2 | 0.923 |
| | 282.2 | 0.597 |
| | 297.9 | 1.22 |
| | 297.9 | 1.34 |
| | 298.0 | 1.57 |
| | 313.8 | 5.24 |
| | 313.9 | 5.17 |
| | 313.9 | 5.46 |
| | 333.8 | 10.0 |
| | 333.8 | 16.9 |
| | 333.9 | 15.5 |

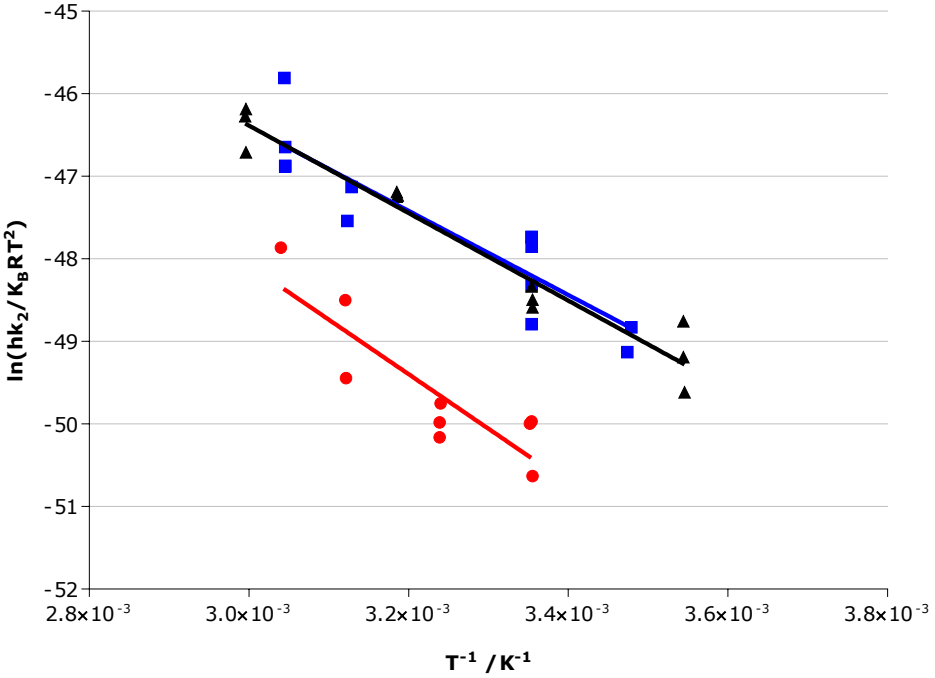


**Fig. S2.** Eyring plot from which the activation parameters were determined for the ethanolysis of diethyl chlorophosphate in acetonitrile with an ethanol-$d_6$ concentration of 0.959 mol $L^{-1}$ at the mole fractions of [bmim][$(CF_3SO_2)_2N$], 0.0 (**red**), 0.4 (**blue**) and 0.7 (**black**).

**Table S5**. Activation parameters for the ethanolysis of diethyl chlorophosphate at different mole fractions of [bmim][$(CF_3SO_2)_2N$] in acetonitrile with an ethanol-$d_6$ concentration of 0.959 mol $L^{-1}$.

| $\chi$ [bmim][$(CF_3SO_2)_2N$] | $\Delta H^{\ddagger}$ / kJ mol$^{-1}$ [a] | $\Delta S^{\ddagger}$ / kJ mol$^{-1}$ [a] |
|---|---|---|
| 0 | 55 ± 12 | -235 ± 38 |
| 0.4 | 42 ± 6 | -259 ± 20 |
| 0.7 | 44 ± 3 | -253 ± 11 |

[a] Uncertainties quoted are derived from the fit of the linear regression.

Rate data for the ethanolysis of diethyl chlorophosphate at different mole fractions of lithium bis(trifluoromethylsulfonyl)imide in ethanol-$d_6$, shown in Fig 3, main text:

**Table S6.** The rate constants for the ethanolysis of diethyl chlorophosphate at different mole fractions of lithium bis(trifluoromethylsulfonyl)imide in ethanol-$d_6$ at 298.2 K. Uncertainties are the standard error of the mean derived from at least three replicate measurements at each mole fraction.

| **Mole Fraction of ionic liquid** | **[ethanol-$d_6$] / mol L$^{-1}$** | **$k_{obs}$ / 10$^{-4}$ s$^{-1}$** | **$k_2$ / 10$^{-6}$ mol L$^{-1}$ s$^{-1}$** | **Average $k_2$ / 10$^{-6}$ mol L$^{-1}$ s$^{-1}$** |
|---|---|---|---|---|
| 0.00 | 16.4 | 1.14 | 6.96 | 7.52 ± 0.32 |
| | | 1.33 | 8.08 | |
| | | 1.24 | 7.52 | |
| 0.61 | 17.9 | 1.04 | 5.81 | 6.13 ± 0.19 |
| | | 1.16 | 6.46 | |
| | | 1.10 | 6.13 | |
| 0.79 | 13.5 | 0.872 | 6.44 | 6.50 ± 0.03 |
| | | 0.883 | 6.52 | |
| | | 0.885 | 6.53 | |
| 0.14 | 12.1 | 0.462 | 3.83 | 3.25 ± 0.49 |
| | | 0.301 | 2.50 | |
| | | 0.300 | 2.48 | |
| 0.16 | 10.7 | 0.167 | 1.56 | 1.58 ± 0.03 |
| | | 0.164 | 1.54 | |
| | | 0.175 | 1.63 | |
| 0.24 | 8.89 | 0.0309 | 0.35 | 0.26 ± 0.06 |
| | | 0.0134 | 0.15 | |
| | | 0.0251 | 0.28 | |

Rate data for the ethanolysis of diethyl chlorophosphate at different mole fractions of [bmim][Cl] in ethanol-$d_6$, shown in Fig 4, main text:

**Table S7.** The rate constants for the ethanolysis of diethyl chlorophosphate at different mole fractions of [bmim][Cl] in ethanol-$d_6$ at 298.2 K. Uncertainties are the standard error of the mean derived from at least three replicate measurements at each mole fraction.

| Mole Fraction of ionic liquid | [ethanol-$d_6$] / mol $L^{-1}$ | $k_{obs}$ / $10^{-4}$ $s^{-1}$ | $k_2$ / $10^{-5}$ mol $L^{-1}$ $s^{-1}$ | Average $k_2$ / $10^{-5}$ mol $L^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| 0 | 16.4 | 0.114 | 0.70 | 0.75 ± 0.03 |
| | | 0.124 | 0.75 | |
| | | 0.133 | 0.81 | |
| 0.04 | 14.6 | 0.204 | 1.40 | 1.41 ± 0.06 |
| | | 0.192 | 1.32 | |
| | | 0.220 | 1.51 | |
| 0.13 | 11.5 | 0.608 | 5.27 | 5.52 ± 0.13 |
| | | 0.653 | 5.65 | |
| | | 0.651 | 5.64 | |
| 0.22 | 8.95 | 0.700 | 7.82 | 8.36 ± 0.28 |
| | | 0.783 | 8.75 | |
| | | 0.774 | 8.52 | |
| 0.39 | 5.31 | 0.409 | 7.70 | 8.27 ± 0.28 |
| | | 0.456 | 8.58 | |
| | | 0.453 | 8.52 | |

Rate data and Eyring plot for the ethanolysis of diethyl chlorophosphate used for the determination of the activation parameters, shown in Table 5, main text:

**Table S8.** The rate constants for the ethanolysis of diethyl chlorophosphate in the presence of the salts [bmim][$(CF_3SO_2)_2N$], lithium bis(trifluoromethylsulfonyl)imide and[bmim][Cl]in ethanol-$d_6$ at various temperatures.

| Mole Fraction of ionic liquid | Temperature / K | [ethanol-$d_6$] / mol $L^{-1}$ | $k_{obs}$ / $10^{-4}$ $s^{-1}$ | $k_2$ / $10^{-5}$ mol $L^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| 0.00 | 277.7 | 16.4 | 0.161 | 0.0979 |
| | 277.7 | | 0.156 | 0.0948 |
| | 277.8 | | 0.136 | 0.0827 |
| | 285.7 | | 0.457 | 0.278 |
| | 285.8 | | 0.437 | 0.266 |
| | 285.9 | | 0.449 | 0.273 |
| | 297.5 | | 1.14 | 0.696 |
| | 297.9 | | 1.33 | 0.808 |
| | 298.0 | | 1.24 | 0.752 |
| | 314.1 | | 4.52 | 2.75 |
| | 314.1 | | 4.73 | 2.88 |
| | 314.2 | | 4.49 | 2.73 |
| 0.21 | 285.7 | 6.85 | 0.787 | 1.15 |
| [bmim][$(CF_3SO_2)_2N$] | 285.8 | | 0.811 | 1.18 |
| | 285.8 | | 0.774 | 1.13 |
| | 298.2 | | 1.88 | 2.75 |
| | 298.2 | | 1.90 | 2.78 |
| | 298.2 | | 1.82 | 2.66 |
| | 308.7 | | 4.24 | 6.20 |
| | 308.8 | | 4.00 | 5.84 |
| | 308.2 | | 3.88 | 5.67 |
| | 320.3 | | 6.14 | 8.97 |
| | 320.3 | | 8.94 | 13.1 |
| | 320.2 | | 8.13 | 11.9 |
| | 328.9 | | 15.3 | 22.4 |
| | 328.9 | | 15.0 | 21.9 |
| | 328.9 | | 11.9 | 17.3 |
| 0.24 | 298.05 | 8.89 | 0.0309 | 0.0347 |
| [Li][$(CF_3SO_2)_2N$] | 298.05 | | 0.0134 | 0.0151 |
| | 298.15 | | 0.0251 | 0.0282 |
| | 313.55 | | 0.112 | 0.126 |
| | 313.65 | | 0.113 | 0.127 |
| | 313.65 | | 0.168 | 0.189 |
| | 323.15 | | 0.325 | 0.365 |
| | 323.15 | | 0.384 | 0.431 |
| | 323.15 | | 0.341 | 0.384 |
| | 332.65 | | 0.569 | 0.640 |
| | 332.65 | | 0.720 | 0.810 |
| | 332.75 | | 0.578 | 0.650 |
| 0.22 | 276.65 | 8.95 | 1.41 | 1.58 |
| [bmim][Cl] | 276.65 | | 1.39 | 1.55 |
| | 276.65 | | 1.26 | 1.41 |
| | 286.75 | | 2.84 | 3.17 |
| | 286.75 | | 2.91 | 3.25 |
| | 286.75 | | 2.85 | 3.19 |
| | 298.15 | | 7.00 | 7.82 |
| | 298.15 | | 7.83 | 8.75 |
| | 298.15 | | 7.62 | 8.52 |
| | 307.25 | | 16.1 | 18.0 |
| | 307.75 | | 15.4 | 17.2 |
| | 307.75 | | 16.4 | 18.3 |
| | 307.75 | | 15.0 | 16.8 |

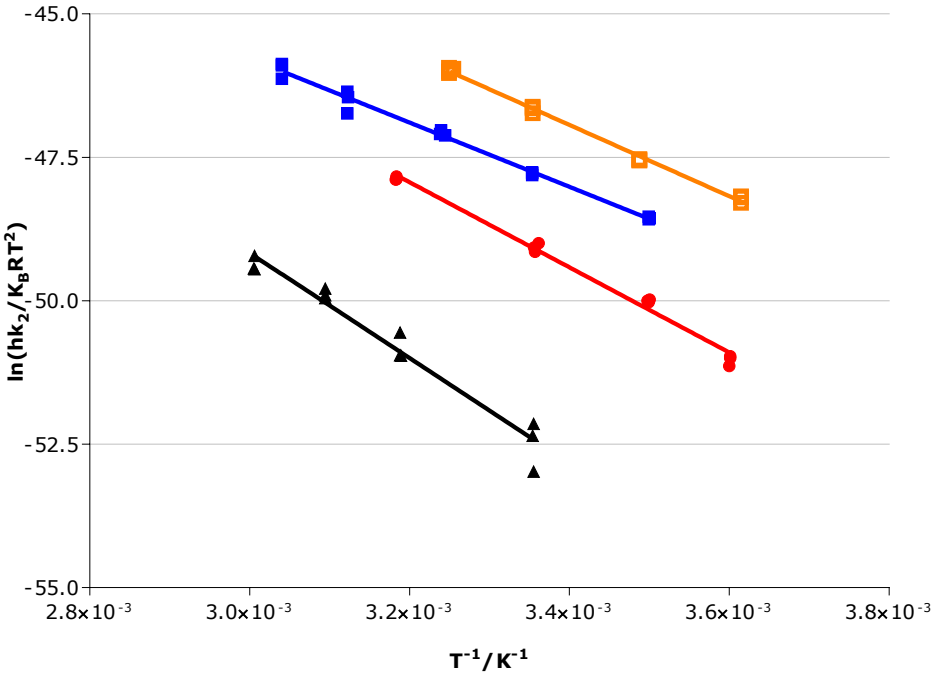


**Fig. S3.** Eyring plot from which the activation parameters were determined for the ethanolysis of diethyl chlorophosphate in neat ethanol-$d_6$ (**red**) and in presence of the salts [bmim][$(CF_3SO_2)_2N$] ($\chi$ = 0.21, **blue**), lithium bis(trifluoromethylsulfonyl)imide ($\chi$ = 0.24, **black**) and [bmim][Cl] ($\chi$ = 0.22, **orange**) in ethanol-$d_6$.