Electronic supporting information for

"Solvent reorganisation as the driving force for rate changes of Menschutkin reactions in an ionic liquid"

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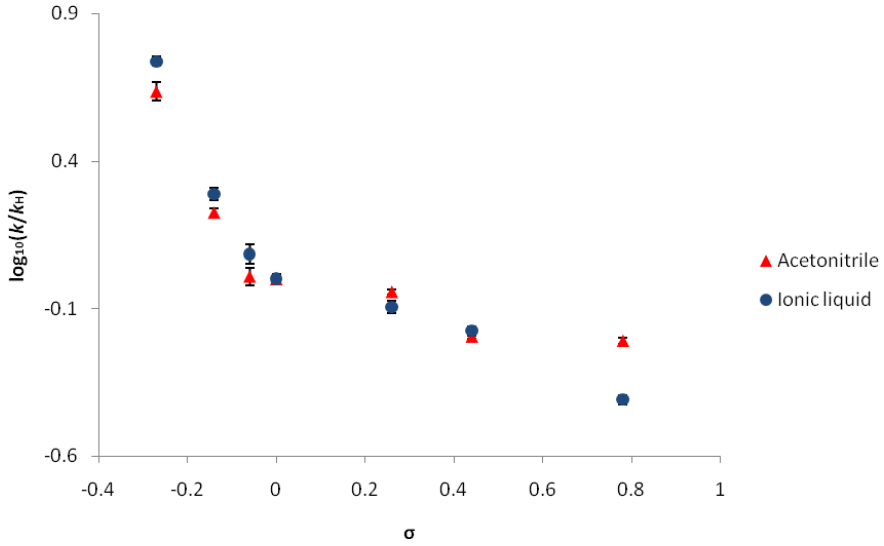
Combined Hammett plot for the Menschutkin reactions carried out at 300.8 K



Combined Hammett plot of the Menschutkin reactions shown in Scheme 1 carried out in both acetonitrile and the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Bmim][N(CF_3SO_2)$_2$]) at 300.8 K. Each point represents the data derived from the average of at least three, and up to six, rate constants and errors are reported as the combined standard deviation of the respective means. Note that the reactions were also carried out at 311.5 K in acetonitrile and 278.1 K in [Bmim][N(CF_3SO_2)$_2$] and the Hammett plots for these experiments are not shown for these non-coinciding temperatures.

Second order rate constants for the Menschutkin reactions of benzyl bromides in acetonitrile

Benzyl bromide	k_2 (300.8 K) / 10^{-4} mol L^{-1} s^{-1}	k_2 (311.5 K) / 10^{-4} mol L^{-1} s^{-1}
1a	41.9 ± 2.85	80.1 ± 0.81
1b	16.3 ± 0.50	33.7 ± 0.17
1c	9.85 ± 0.66	19.0 ± 0.12
1d	9.66 ± 0.13	18.6 ± 0.30
1e	8.74 ± 0.12	17.2 ± 0.69
1f	6.16 ± 0.73	15.2 ± 0.23
1g	5.96 ± 0.10	11.6 ± 0.33

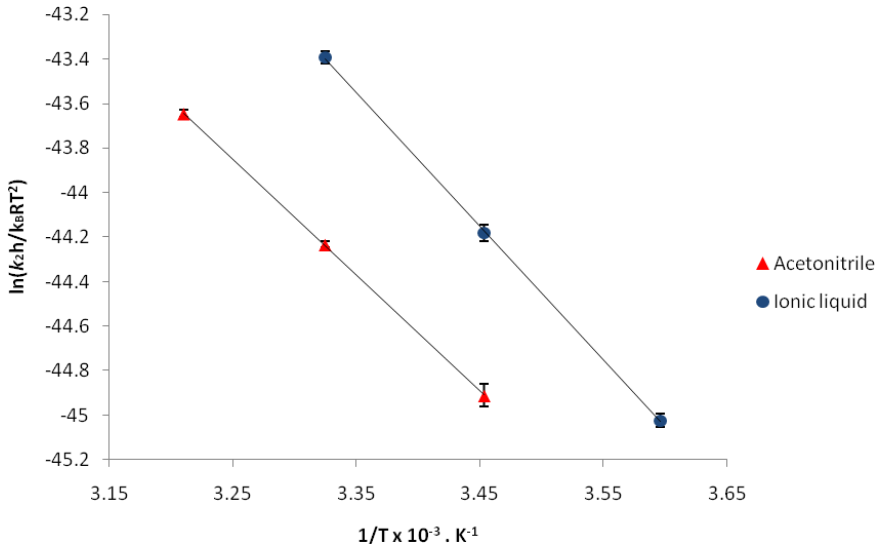
Second order rate constants calculated for the Menschutkin reactions of benzyl bromides with pyridine in acetonitrile at temperatures other than 289.6 K. Errors are reported as standard deviations.

Second order rate constants for the Menschutkin reactions of benzyl bromides in [Bmim][$N(CF_3SO_2)_2$]

Benzyl bromide	k_2 (278.1 K) / 10^{-4} mol L^{-1} s^{-1}	k_2 (300.8 K) / 10^{-4} mol L^{-1} s^{-1}
1a	22.1 ± 2.00	122 ± 2.69
1b	7.65 ± 0.23	43.5 ± 1.74
1c	4.06 ± 0.23	27.1 ± 1.94
1d	3.75 ± 0.12	22.4 ± 0.65
1e	2.89 ± 0.12	18.0 ± 0.64
1f	2.19 ± 0.08	14.9 ± 0.35
1g	1.52 ± 0.05	8.75 ± 0.19

Second order rate constants calculated for the Menschutkin reactions of benzyl bromides with pyridine in [Bmim][$N(CF_3SO_2)_2$] at temperatures other than 289.6 K. Errors are reported as standard deviations.

A typical Eyring plot from which the activation parameters in Table 2 and 3 are derived



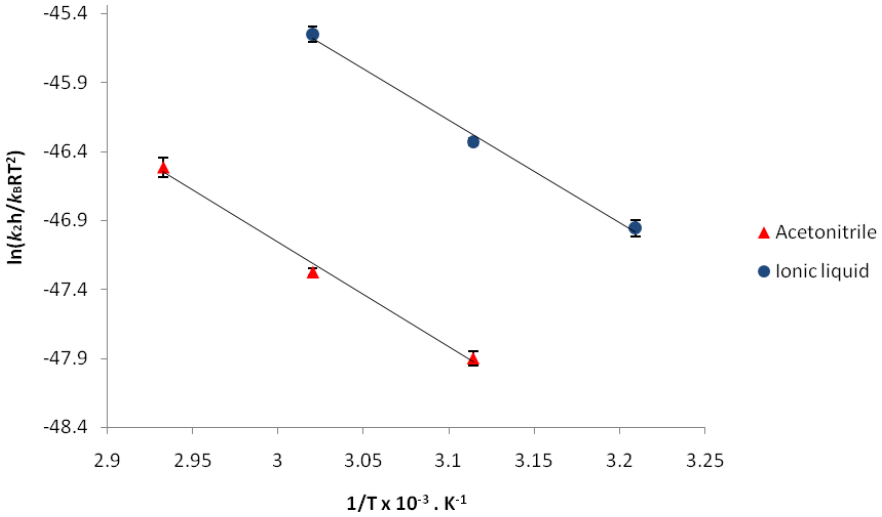
The activation parameters of the Menschutkin reactions of benzyl bromides with pyridine were calculated by fitting temperature-dependent kinetic data to the Eyring eqution for both acetonitrile and [Bmim][$N(CF_3SO_2)_2$]. Each point is the data derived from the average of at least three, and up to six, second order rate constants and the errors are reported as standard deviations from the means. The small range of temperatures shown here is limited by time scale of NMR spectroscopy at the maximum and the practicality to monitor long experiments at the minimum. It is worth noting that, even though the range of temperatures is small, the activation parameters obtained were consistent across the series of substituents.

Second order rate constants for the Menschutkin reactions of benzyl chloride

Temperature / K	k_2 (Acetonitrile) / 10^{-5} mol L^{-1} s^{-1}	k_2 ([Bmim][$N(CF_3SO_2)_2$]) / 10^{-5} mol L^{-1} s^{-1}
311.6	-	6.80 ± 0.40
321.1	2.81 ± 0.15	13.5 ± 0.34
331.1	5.59 ± 0.15	31.3 ± 1.73
341.0	12.7 ± 0.87	-

Second order rate constants for the Menschutkin reaction of benzyl chloride with pyridine in acetonitrile and [Bmim][$N(CF_3SO_2)_2$]. Errors are reported as standard deviations.

Eyring plot from which the activation parameters in Table 5 are derived



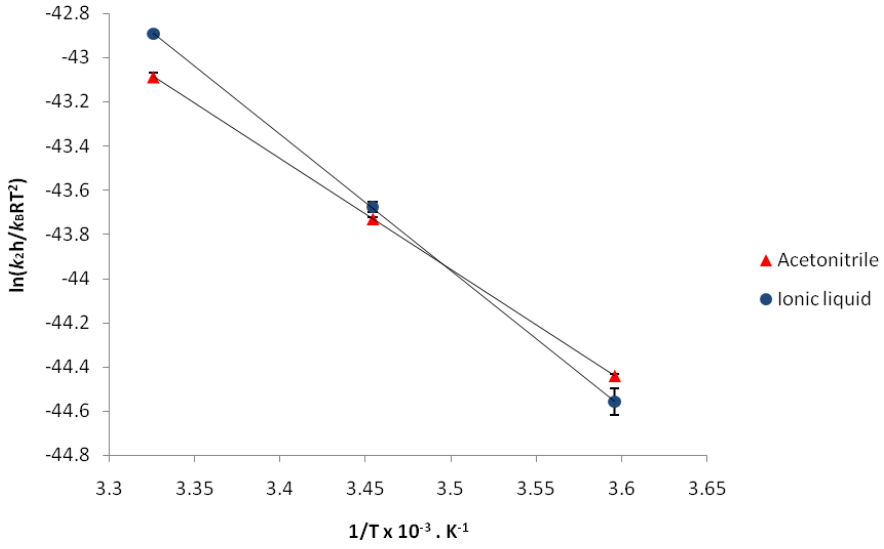
The activation parameters of the Menschutkin reaction of benzyl chloride with pyridine was calculated by fitting temperature-dependent kinetic data to the Eyring eqution for both acetonitrile and [Bmim][$N(CF_3SO_2)_2$]. Each point is the data derived from the average of at least three, and up to six, second order rate constants and the errors are reported as standard deviations from the means.

Second order rate constants for the Menschutkin reactions of benzyl iodide

Temperature / K	k_2 (Acetonitrile) / 10^{-4} mol L^{-1} s^{-1}	k_2 ([Bmim][$N(CF_3SO_2)_2$]) / 10^{-4} mol L^{-1} s^{-1}
278.1	6.70 ± 0.07	5.96 ± 0.09
289.5	14.8 ± 0.11	15.6 ± 0.11
300.7	30.3 ± 0.59	36.9 ± 0.21

Second order rate constants for the Menschutkin reaction of benzyl iodide with pyridine in acetonitrile and [Bmim][$N(CF_3SO_2)_2$]. Errors are reported as standard deviations.

Eyring plot from which the activation parameters in Table 6 are derived



The activation parameters of the Menschutkin reaction of benzyl iodide with pyridine was calculated by fitting temperature-dependent kinetic data to the Eyring eqution for both acetonitrile and [Bmim][$N(CF_3SO_2)_2$]. Each point is the data derived from the average of at least three, and up to four, second order rate constants and the errors are reported as standard deviations from the means.