An old reaction in new media: Kinetic study of a Platinum(II) substitution reaction in ionic liquids

Supplementary Information

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Characterization of the ionic liquids

[C_4C_1im][NTf_2] – The ionic liquid was prepared according to a literature procedure.[17]

δ_H: (400 MHz, DMSO-d_6)/ppm 8.78 (1H, s, N_2CH), 7.40 and 7.35 (2H, m, 2NCH), 4.20 (2H, t, $NCH_2(CH_2)_2CH_3$), 3.86 (3H, s, NCH_3), 1.88 (2H, quintet, $NCH_2CH_2CH_2CH_3$), 1.35 (2H, sextet, $NCH_2CH_2CH_2CH_3$) and 0.95 (3H, t, $N(CH_2)_3CH_3$)

m/z (FAB+): 558 ($[(C_4C_1im)_2N(SO_2CF_3)_2]^+$, 45%) and 139 ($[C_4C_1im]^+$, 100)

m/z (FAB−): 280 ($[N(SO_2CF_3)_2]^-$, 100%).

[C_4C_1py][NTf_2] – The ionic liquid was prepared according to a literature procedure.[17]

δ_H: (400 MHz, DMSO-d_6)/ppm 3.56–3.36 (4H, m, $N(CH_2)_2$), 3.34–3.24 (2H, m, $NCH_2(CH_2)CH_3$), 2.99 (3H, s, NCH_3), 2.10 (4H, br. s, $NCH_2(CH_2)_2CH_3$), 1.70 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.33 (2H, sextet, $N(CH_2)_2CH_2CH_3$) and 0.94 (3H, t, $N(CH_2)_3CH_3$)

m/z (FAB+): 564 ($[(C_4C_1py)_2N(SO_2CF_3)_2]^+$, 30%) and 142 ($[C_4C_1py]^+$, 100%)

m/z (FAB−): 280 ($[N(SO_2CF_3)_2]^-$, 100%).

[C_4C_1py][OTf] – The ionic liquid was prepared according to a literature procedure.[17]

δ_H: (400 MHz, DMSO-d_6)/ppm 3.55–3.35 (4H, m, $N(CH_2)_2$), 3.33–3.23 (2H, m, $NCH_2(CH_2)CH_3$), 2.97 (3H, s, NCH_3), 2.0 (4H, br. s, $NCH_2(CH_2)_2CH_3$), 1.70 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.30 (2H, sextet, $N(CH_2)_2CH_2CH_3$) and 0.94 (3H, t, $N(CH_2)_3CH_3$)

m/z (FAB+): 433 ($[(C_4C_1py)_2(CF_3SO_3)]^+$, 5%) and 142 ($[C_4C_1py]^+$, 100%)

m/z (FAB−): 440 ($[(C_4C_1py)(CF_3SO_3)_2]^-$, 5%) 149 [$(CF_3SO_3)^-$, 100%].

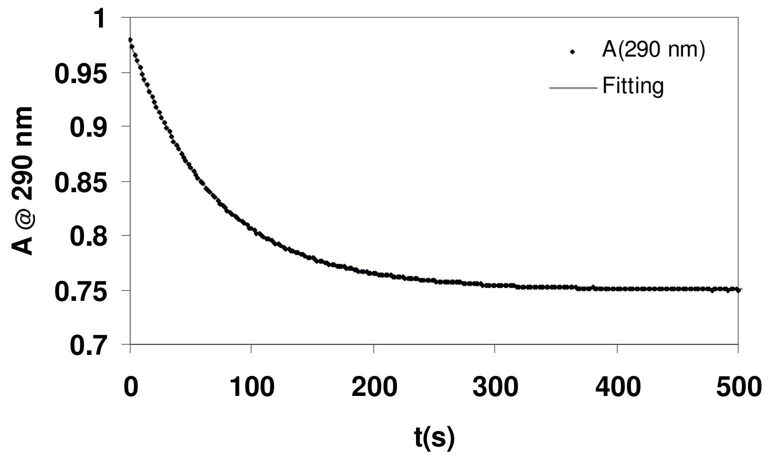
$[(C_1OC_2)C_1im][NTf_2]$ – The ionic liquid was donated by a colleague.

δ_H: (400 MHz, DMSO-d_6)/ppm 9.10 (1H, s, N_2CH), 7.75 (2H, m, 2NC*H*), 4.35 (2H, t, $NCH_2CH_2OCH_3$), 3.87 (3H, s, NCH_3), 3.65 (2H, t, $NCH_2CH_2OCH_3$), 3.35 (3H, s, OCH_3) and 2.50 (2H, t, NCH_2CH_2O)

m/z (FAB+): 562 ($\{[(C_3OC_1)C_1im]_2([N(SO_2CF_3)_2]\}^+$, 15%) 282 $\{[(C_3OC_1)C_1im]_2\}^{2+}$, 10%) and 139 ($[C_4C_1im]^+$, 100)

m/z (FAB−): 280 ($[N(SO_2CF_3)_2]^-$, 100%).

Kinetic studies



Kinetic trace of the reaction $[Pt(dpma)Cl]^+ + SAc^- \rightleftharpoons [Pt(dpma)SAc]^+ + Cl^-$ in $[C_4C_1py][NTf_2]$ at 25 °C. Concentrations of $[Pt(dpma)Cl]^+ = 0.99\text{x}10^{-3}$ M and KSAc = $39.0\text{x}10^{-4}$ M.

Plots of k_{obs} (s^{-1}) *vs*. [SAc^-] (M) for $[Pt(bpma)Cl]^+ \sim 1 \times 10^{-4}$ M at 25 ^oC

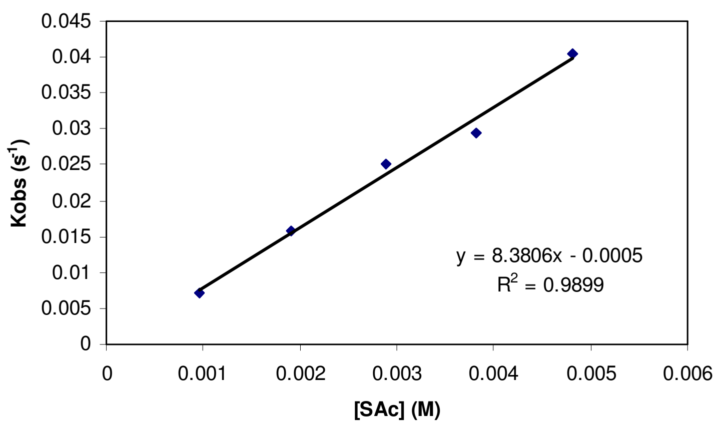


Fig S1 – In $[C_4C_1im][NTf_2]$

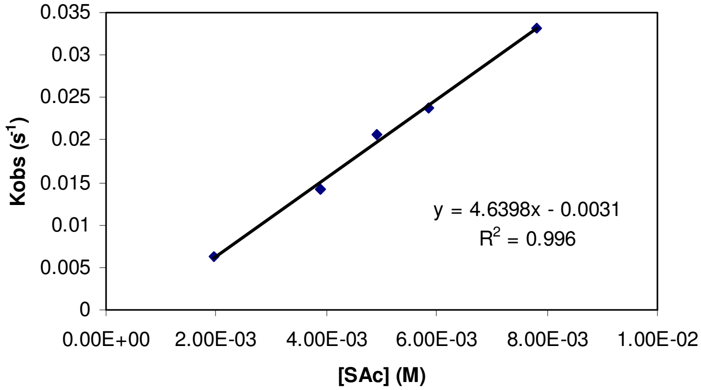


Fig S2 – In $[C_4C_1py][NTf_2]$

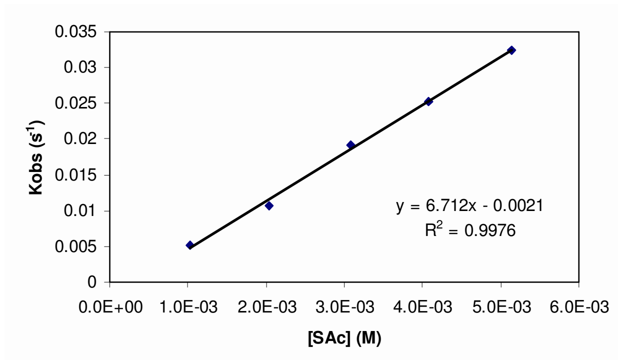


Fig S3 – In $[C_4C_1py][OTf]$

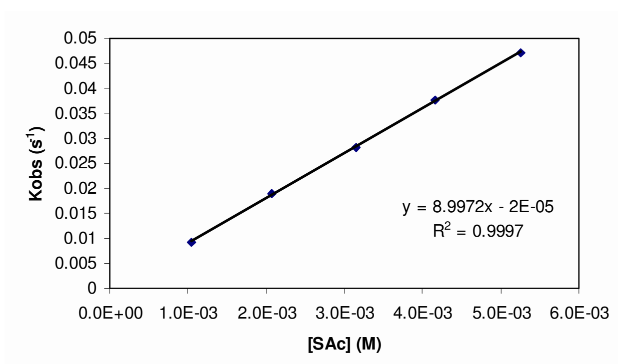


Fig S4 – In $[(C_1OC_2)C_1im][NTf_2]$

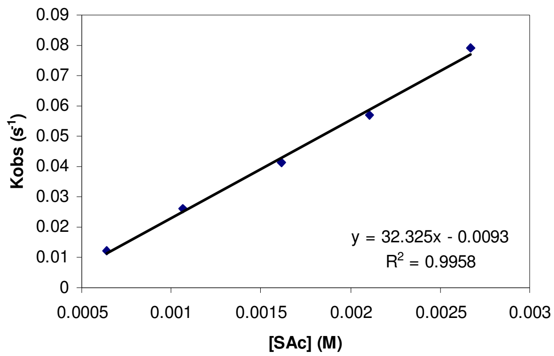


Fig S5 – In H_2O

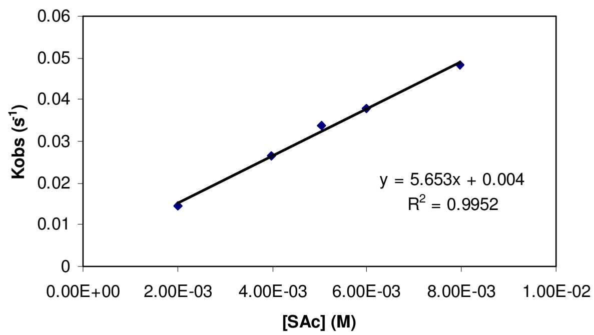


Fig S6 – In DMSO

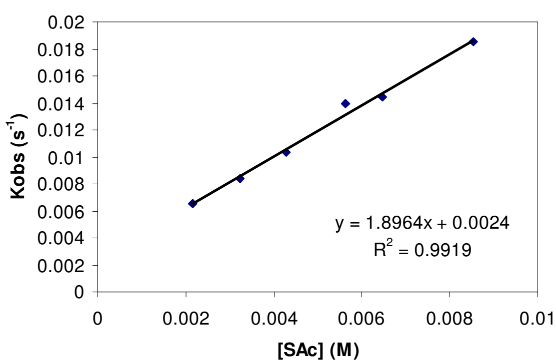


Fig S7 – In MeOH

Eyring Plots

Plots of ln (k_{obs}/T) *vs*. 1/T for $[Pt(bpma)Cl]^+$ ~ 1 × 10^{-4} M:

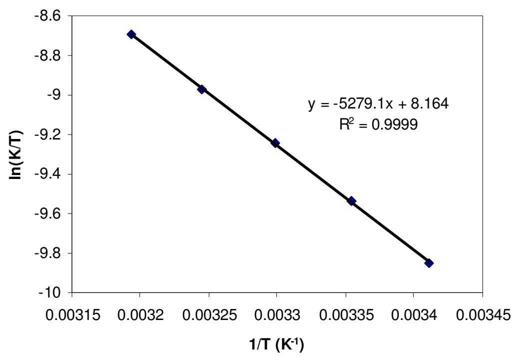


Fig S8 – In $[C_4C_1im][NTf_2]$; [Pt]=9.00x10^{-5}M and [SAc]=2.89x10^{-3}M

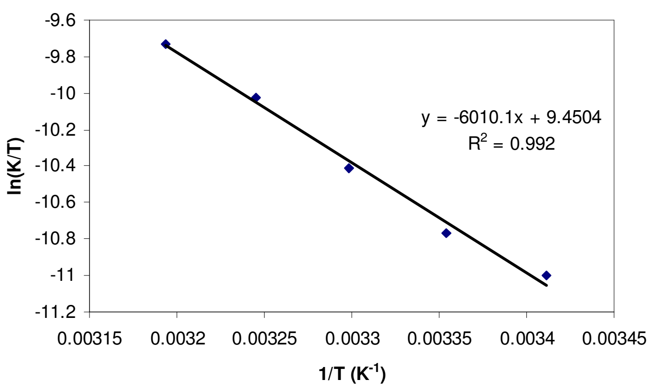


Fig S9 – In $[C_4C_1py][NTf_2]$; [Pt]=9.90x10^{-5}M and [SAc]=1.95x10^{-3}M

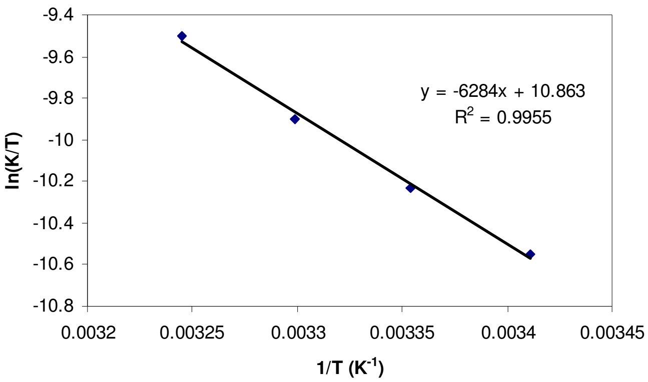


Fig S10 – In $[C_4C_1py][OTf]$; $[Pt]=1.09x10^{-4}M$ and $[SAc]=2.04x10^{-3}M$

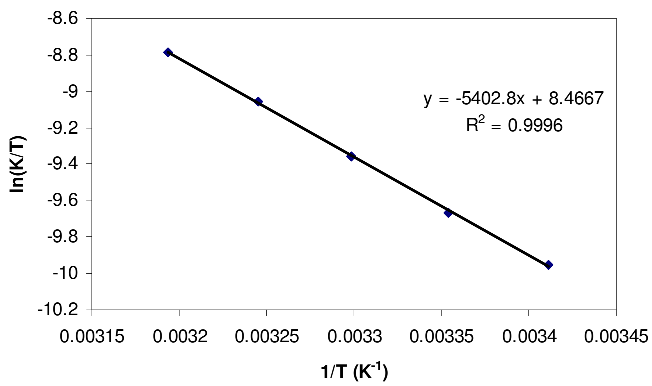


Fig S11 – In $[(C_1OC_2)C_1im][NTf_2]$; $[Pt]=1.04x10^{-4}M$ and $[SAc]=2.08x10^{-3}M$

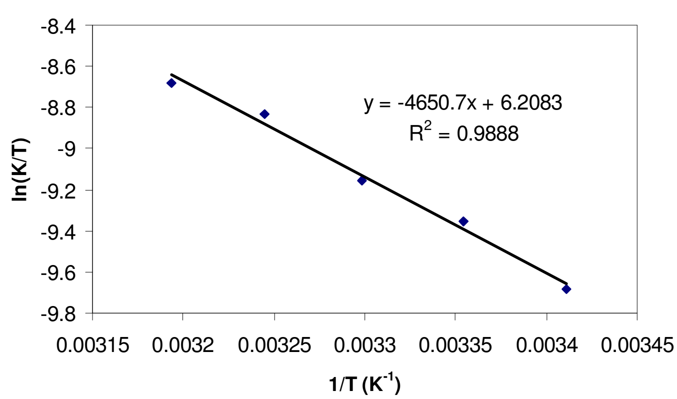


Fig S12 – In H_2O; $[Pt]=3.96x10^{-5}M$ and $[SAc]=1.06x10^{-3}M$

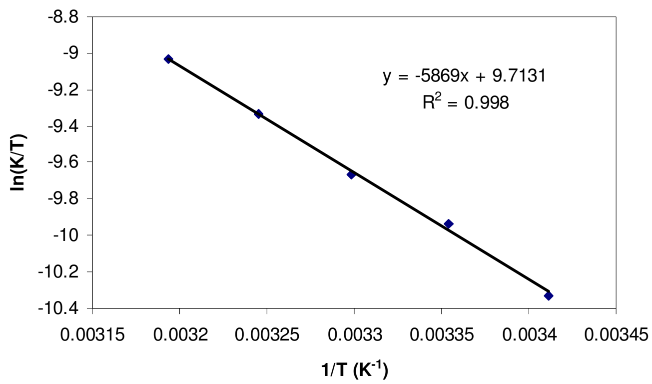


Fig S13 – In DMSO; [Pt]=8.916x10^{-5}M and [SAc]=1.99x10^{-3}M

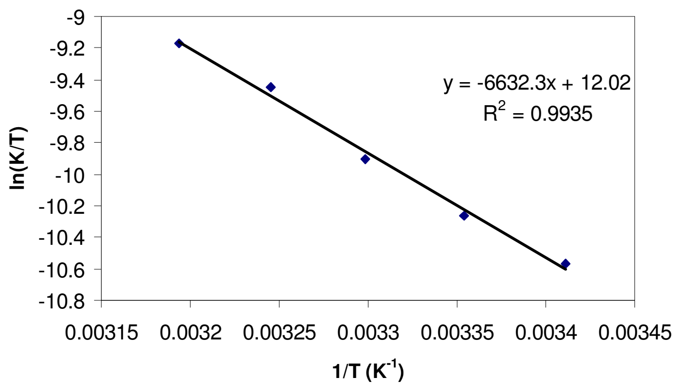


Fig S14 – In MeOH; [Pt]=8.986x10^{-5}M and [SAc]=4.27x10^{-3}M

Table S1 – k_{obs} at various temperatures-

Solvent	**T (ºC)**	**K_{obs} (×10^2) / s^{-1}**
MeOH	20	0.755
[SAc] = 4.27 ×10^{-3}M	25	1.04
[Pt] = 8,98 ×10^{-5}M	30	1.51
	35	2.43
	40	3.26
H_2O	20	1.82
[SAc] = 1.06 ×10^{-3}M	25	2.59
[Pt] = 3.96 ×10^{-5}M	30	3.20
	35	4.51
	40	5.31
DMSO	20	0.959
[SAc] = 1.99 ×10^{-3}M	25	1.45
[Pt] = 8.91 ×10^{-5}M	30	1.93
	35	2.72
	40	3.75
[(C_1OC_2)C_1im][NTf_2]	20	1.39
[SAc] = 2.08×10^{-3}M	25	1.89
[Pt] = 1.04 ×10^{-4}M	30	2.62
	35	3.59
	40	4.78
[C_4C_1im][NTf_2]	20	1.55
[SAc]=2.89 ×10^{-3}M	25	2.15
[Pt]=9.00×10^{-5}M	30	2.93
	35	3.91
	40	5.25
[C_4C_1py][NTf_2]	20	0.491
[SAc]=1.95 ×10^{-3}M	25	0.630
[Pt]=9.90 ×10^{-5}M	30	0.910
	35	1.36
	40	1.87
[C_4C_1py][OTf]	20	0.767
[SAc]=2.04 ×10^{-3}M	25	1.07
Pt]=1.09 ×10^{-4}M	30	1.52
	35	2.30