

INFLUENCE OF THE IONIC LIQUID ON RATE AND MECHANISM OF REACTION OF P-NITROPHENYL ACETATE WITH SECONDARY ALICYCLIC AMINES

Daniela Millán*¹, Mabel Rojas¹, Paulina Pavez¹, Mauricio Isaacs², Carlos Diaz² and José G. Santos¹

¹Departamento de Fisicoquímica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile.

² Departamento de Química Inorgánica, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile

Electronic supplementary information

Table of contents	
Table S1 : Pseudo-first-order rate constants (k_{obs}) for the reaction of NPA (1) with SA amines in [Bmim]BF ₄ .	S2
Table S2 : Pseudo-first-order rate constants (k_{obs}) for the reaction of NPA (1) with piperidine in different ionic liquids.	S3
Table S3 : Experimental conditions and pseudo-first-order rate constants for the reaction of NPA (1) with piperidine in organic solvents at 25°C.	S4
Figure S1 : Bronsted type plot using relatives basicities (K_{rel}) of alicyclic amines in [Bmim]BF ₄ .	S5
Figure S2 : Voltammogram of piperidine+ strong acid HOTf in [Bmim]BF ₄	S5
Figure S3 : Voltammogram of morpholine+ strong acid HOTf in [Bmim]BF ₄	S6

Tables

Table S-1. Pseudo-first-order rate constants (k_{obs}) for the reaction of NPA (**1**) with SA amines in [Bmim]BF₄.

Piperidine	
[A] _T / [M]	k_{obs} / s ⁻¹
0,0087	0,01665
0,01087	0,0308
0,01304	0,03747
0,01522	0,05661
0,01739	0,06475
0,01956	0,08272
0,02174	0,09036

Formylpiperazine	
[A] _T / [M]	k_{obs} / s ⁻¹
0,02174	7,8E-4
0,04348	0,00164
0,06522	0,00251
0,08696	0,00336

Morpholine	
[A] _T / [M]	k_{obs} / s ⁻¹
0,0087	1,1E-4
0,01087	0,00153
0,01304	0,00236
0,01522	0,00437
0,01739	0,00493
0,02174	0,00712

1-(2-hydroxyethyl)-piperazine	
[A] _T / [M]	k_{obs} / s ⁻¹
0,0087	0,00393
0,01087	0,00568
0,01304	0,0079
0,01522	0,00966
0,01739	0,01123
0,01956	0,01296

Table S-2. Pseudo-first-order rate constants (k_{obs}) for the reaction of NPA (1) with piperidine in different ionic liquids.

[Bmim]BF ₄	
[A] _T / [M]	k_{obs} / s ⁻¹
0,0087	0,01665
0,01087	0,0308
0,01304	0,03747
0,01522	0,05661
0,01739	0,06475
0,01956	0,08272
0,02174	0,09036

[Bm ₂ im]BF ₄	
[A] _T / [M]	k_{obs} / s ⁻¹
0,0087	0,01271
0,01304	0,01902
0,01522	0,0214
0,01739	0,02465
0,01956	0,02605
0,02174	0,02851

[Bm ₂ im]ntf ₂	
[A] _T / [M]	k_{obs} / s ⁻¹
0,0087	0,01728
0,01087	0,02407
0,01304	0,03134
0,01522	0,03902
0,01739	0,04515
0,01956	0,05236
0,02174	0,05858

[Bmim]DCA	
[A] _T / [M]	k_{obs} / s ⁻¹
0,0087	0,03715
0,01087	0,04909
0,01304	0,05144
0,01522	0,06326
0,01739	0,06873
0,01956	0,07979
0,02174	0,08711

[Bmim]PF ₆	
[A] _T / [M]	k_{obs} / s ⁻¹
0,0087	0,00458
0,01087	0,00554
0,01304	0,00617
0,01522	0,00662
0,01956	0,00866
0,02174	0,00893

Table S-3. Experimental conditions and pseudo-first-order rate constants for the reaction of NPA (1) with piperidine in organic solvents at 25°C.

Acetonitrile		Ethanol	
[A] _T / [M]	<i>k</i> _{obs} / s ⁻¹	[A] _T / [M]	<i>k</i> _{obs} / s ⁻¹
0,0087	0,01868	0,0087	0,00443
0,01087	0,02379	0,01087	0,00507
0,01304	0,02831	0,01304	0,00619
0,01522	0,03331	0,01522	0,00691
0,01739	0,03864	0,01739	0,00793
0,01956	0,0433	0,02174	0,00976
0,02174	0,04839		
Dimethylsulphoxide		Dichlorometane	
[A] _T / [M]	<i>k</i> _{obs} / s ⁻¹	[A] _T / [M]	<i>k</i> _{obs} / s ⁻¹
0,0162	0,15855	0,00806	6,0963E-4
0,0243	0,48983	0,0322	0,00358
0,0322	0,83393	0,0522	0,00583
		0,0681	0,00838
		0,088	0,0117
Heptane		Acetone	
[A] _T / [M]	<i>k</i> _{obs} / s ⁻¹	[A] _T / [M]	<i>k</i> _{obs} / s ⁻¹
0,0522	9,1432E-4	0,0087	0,01333
0,0681	0,00173	0,01087	0,02008
0,088	0,00268	0,01304	0,02564
0,1077	0,00366	0,01522	0,03153
0,1274	0,00463		
Methanol		Tetrahydrofurane	
[A] _T / [M]	<i>k</i> _{obs} / s ⁻¹	[A] _T / [M]	<i>k</i> _{obs} / s ⁻¹
0,00806	0,00168	0,0087	0,0123
0,0322	0,00371	0,01087	0,01593
0,0522	0,00605	0,01522	0,02197
0,0681	0,00772	0,01956	0,02784
		0,02174	0,03305

Figures

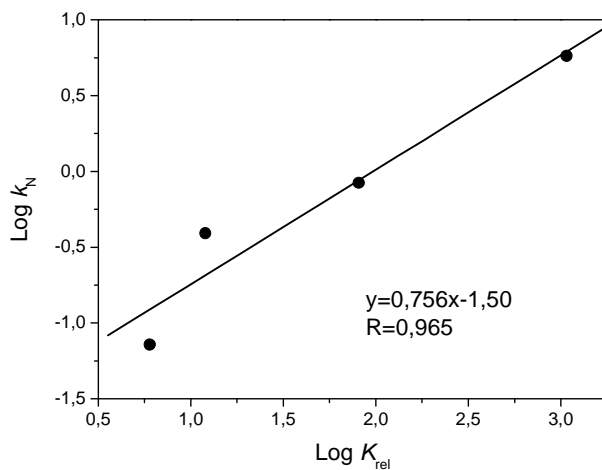


Figure S-1 : Bronsted type plot using relative basicities (K_{rel}) of alicyclic amines in [Bmim]BF₄.

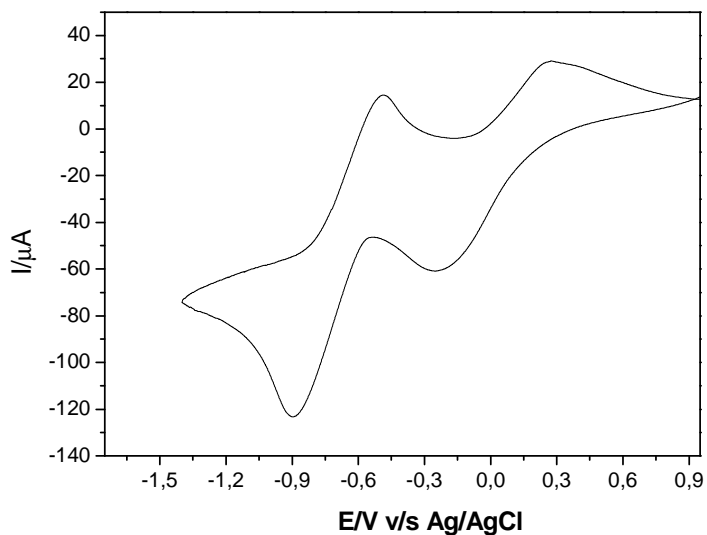


Figure S-2 : Voltammogram of piperidine (0.046M) in [Bmim]BF₄ (0.02Vs⁻¹) + strong acid HOTf (0.23M).

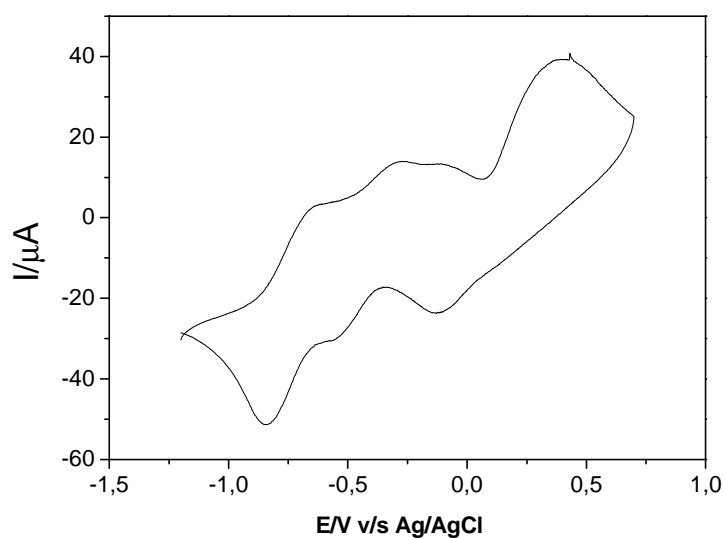


Figure S-3 : Voltammogram of morpholine (0.046M) in [Bmim]BF₄ (0.02 V s^{-1}) + strong acid HOTf (0.23M).