Supporting Information

The Interplay of Acidity and Ionic Liquid Structure on the Outcome of an Heterocyclic Rearrangement reaction

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Calculation details

The ion pair formation equilibrium can be written as

$$4\text{-NA} + HA \leftrightarrows 4\text{-NAH}^+A^-$$

where 4-NA represents 4-nitroaniline, HA the acid under investigation, and $4NAH^+ A^-$ is the ion pair formed.

The equilibrium constant will be given by:

$$K_{ass} = \frac{[4\text{-NAH}^{\oplus}\ A^{\ominus}]}{[HA]\,[4\text{-NA}]} \qquad (1)$$

The analytical concentration of 4-nitroaniline can be defined as:

$$[4\text{-NA}]_t = [4\text{-NA}] + [4\text{-NAH}^+A^-] = C_{4\text{-NA}} \qquad (2)$$

The analytical concentration of acid can be defined as:

$$[HA]_t = [HA] + [4\text{-NAH}^+A^-] = C_a \qquad (3)$$

The absorbance of a measurement solution will be equal to:

$$A = A_{4\text{-NA}} + A_{4\text{-NAHA}} = b\cdot\varepsilon_{4NA}\cdot[4\text{-NA}] + b\cdot\varepsilon_{4\text{-NAHA}}\cdot[4\text{-NAH}^+A] \qquad (4)$$

The absorbance of the 4-nitroaniline solution will be equal to:

$$A_0 = b\cdot\varepsilon_{4\text{-NA}}\cdot C_{4\text{-NA}} \qquad (5)$$

The absorbance variation as a consequence of the acid addition will be:

$$\Delta A = A_0 - A = b\cdot\varepsilon_{4\text{-NA}}\cdot C_{4\text{-NA}} - b\cdot\varepsilon_{4\text{-NAHA}}\cdot[4\text{-NAH}^+A^-] + b\cdot\varepsilon_{4\text{-NA}}\cdot[4\text{-NAH}^+A^-] \qquad (6)$$

Considering Eq. 2 , the above equation can be written as:

$$\Delta A = b\cdot\Delta\varepsilon\cdot[4\text{-NAH}^+A^-] \qquad (7)$$

where $\Delta\varepsilon = \varepsilon_{4\text{-NA}} - \varepsilon_{4\text{-NAHA}}$

From Eq. 1 the following expression is obtained:

$$[4\text{-NAH}^{\oplus}\ A^{\ominus}] = \frac{C_{4\text{-NA}} * K_{ass} * [HA]}{1 + K_{ass} * [HA]} \qquad (8)$$

By substitution in Eq. 7, it can be written as:

$$\Delta A = \frac{b * \Delta\varepsilon * C_{4\text{-NA}} * K_{ass} * [HA]}{1 + K_{ass} * [HA]} \qquad (9)$$

In solution of ILs, K_{ass} was determined by non-linear fitting the following equation:

$$\Delta A = \frac{b * \Delta\varepsilon * C_{4\text{-NA}} * K_{ass} * ([HA]\text{-}a)}{1 + K_{ass} * ([HA]\text{-}a)} \qquad (10)$$

K_{ass} values reported in Table S1 where obtained by estimating the concentration of free HA by an iterative method applied to equations 1,2 and 3 until differences in K_{ass} values lower than 5% were calculated.

Table S1. Equilibrium association constant K_{ass} (M^{-1}) at 298.1 K, between 4-nitoraniline and sulfonic acids.

	MSA	***p*-TSA**	**TFMSA**
1,4-Dioxane	[a]	[a]	310 ± 30
Methanol	17 ± 1	27 ± 3	26 ± 3
[bmim][BF_4]	60 ± 11	65 ± 5	190 ± 18
[bmim][PF_6]	100 ± 16	800 ± 100	440 ± 60
[bmim][SbF_6]	61 ± 9	250 ± 20	1800 ± 400
[bmim][NTf_2]	450 ± 40	2500 ± 240	7400 ± 100
[bmpyrr][NTf_2]	270 ± 40	630 ± 100	2400 ± 400
[bm_2im][NTf_2]	140 ± 20	540 ± 60	4000 ± 1000

[a] Spectroscopic variations were too low to obtain an acceptable value for K_{ass}.

Table S2. Second order kinetic constants k_{II} (s^{-1} M^{-1}) for the **1 →2** rearrangement reaction at 298 K.

	TCA	**TFA**	**MSA**	***p*-TSA**	**TFMSA**
1,4-Dioxane	*a*	*a*	$(4.8 \pm 0.2)\cdot10^{-3}$	$(1.5 \pm 0.1)\cdot10^{-2}$	1.6 ± 0.2
Methanol	$(7.3 \pm 0.5)\cdot10^{-4}$	$(6.8 \pm 0.4)\cdot10^{-4}$	$(2.9 \pm 0.1)\cdot10^{-2}$	$(3.7 \pm 0.2)\cdot10^{-2}$	$(3.2 \pm 0.1)\cdot10^{-2}$
[bmim][BF_4]	$(5.0 \pm 0.3)\cdot10^{-3}$	$(7.0 \pm 0.2)\cdot10^{-3}$	0.42 ± 0.03	1.7 ± 0.1	3.7 ± 0.3
[bmim][PF_6]	$(1.23 \pm 0.09)\cdot10^{-3}$	$(1.06 \pm 0.06)\cdot10^{-2}$	1.30 ± 0.05	2.9 ± 0.2	*b*
[bmim][SbF_6]	$(6.9 \pm 0.3)\cdot10^{-3}$	$(5.4 \pm 0.4)\cdot10^{-3}$	0.47 ± 0.03	1.52 ± 0.05	*b*
[bmim][NTf_2]	$(1.00 \pm 0.13)\cdot10^{-3}$	$(2.2 \pm 0.2)\cdot10^{-3}$	1.11 ± 0.07	3.3 ± 0.1	*b*
[bmpyrr][NTf_2]	$(9.9 \pm 0.7)\cdot10^{-3}$	$(2.75 \pm 0.03)\cdot10^{-3}$	2.8 ± 0.1	3.6 ± 0.2	*b*
[bm_2im][NTf_2]	$(5.9 \pm 0.4)\cdot10^{-3}$	$(6.2 \pm 0.6)\cdot10^{-3}$	2.0 ± 0.1	2.7 ± 0.2	*b*

[a] Reaction too slow to determine kinetic constants. [b] Reaction too fast to determine kinetic constants.

Table S3. Absorbance variations as a function of acid concentration, in the presence of 4-NA, in 1,4-dioxane at 298.1 K for TMSA.

1,4-dioxane	
TFMSA	
Concentration (M)	**ΔA**
0	0
0.000608	0.0697
0.000790	0.148
0.00122	0.245
0.00243	0.348
0.00365	0.455
0.00487	0.561
0.00583	0.594
0.00734	0.621
0.00974	0.683
0.0128	0.712
0.0170	0.718
0.0213	0.733

Table S4. Absorbance variations as a function of acid concentration, in the presence of 4-NA, in methanol, at 298.1 K for sulfonic acids.

Methanol	
MSA	
Concentration (M)	**ΔA**
-	0
0.00232	0.0317
0.00696	0.0583
0.0116	0.144
0.0185	0.1899
0.0232	0.264
0.0289	0.291
0.0465	0.383
0.0578	0.459
0.0869	0.496
0.115	0.590
0.139	0.617
0.185	0.642
0.232	0.682
***p*-TSA**	
-	0
0.00193	0.0651
0.00386	0.0827
0.00565	0.0955
0.00773	0.143
0.0193	0.232
0.0282	0.303
0.0386	0.387
0.0565	0.443
0.0808	0.527
TFMSA	
-	0
0.00193	0.0651
0.00386	0.0827
0.00565	0.0955
0.00773	0.143
0.0193	0.232
0.0282	0.303
0.0386	0.387
0.0565	0.443
0.0808	0.527

Table S5. Absorbance variations as a function of acid concentration, in the presence of 4-NA, in [bmim][BF_4] at 298.1 K for sulfonic acids.

[bmim][BF_4]	
MSA	
Concentration (M)	**ΔA**
0.0130	0.0990
0.0158	0.249
0.0169	0.288
0.0226	0.359
0.0282	0.503
0.0395	0.597
0.0452	0.691
0.0565	0.731
0.0740	0.735
0.0904	0.791
***p*-TSA**	
0.00414	0.0234
0.00643	0.0941
0.00804	0.189
0.00965	0.219
0.0121	0.307
0.0144	0.365
0.0161	0.428
0.0193	0.479
0.0241	0.523
0.0322	0.582
0.0402	0.667
0.0483	0.687
0.0603	0.732
0.0804	0.751
TFMSA	
0.00582	0
0.00730	0.0651
0.00852	0.0827
0.00973	0.0955
0.0121	0.143
0.0146	0.232
0.0170	0.303
0.0212	0.387
0.0242	0.443
0.0298	0.527
0.0341	0.831
0.0426	0.838

Table S6. Absorbance variations as a function of acid concentration, in the presence of 4-NA, in [bmim][PF_6] at 298.1 K for sulfonic acids.

[bmim][PF_6]	
MSA	
Concentration (M)	**ΔA**
-	0
0.00160	0.111
0.00273	0.144
0.00362	0.187
0.00549	0.292
0.00701	0.310
0.00825	0.430
0.0109	0.432
0.0120	0.511
0.0164	0.627
0.0211	0.690
0.0274	0.681
0.0351	0.732
0.0439	0.738
0.0549	0.726
***p*-TSA**	
-	0
0.000154	0.135
0.000304	0.196
0.000736	0.301
0.00127	0.384
0.00152	0.379
0.00255	0.480
0.00500	0.547
0.00762	0.617
0.0102	0.680
0.0161	0.716
0.0191	0.682
0.0191	0.754
0.0255	0.680
TFMSA	
-	0
0.00313	0.589
0.000626	0.169
0.00156	0.442
0.00626	0.780
0.00939	0.901
0.0152	0.922
0.000939	0.379
0.00469	0.699
0.00782	0.815
0.0182	0.948
0.0126	0.886
0.0220	0.959

Table S7. Absorbance variations as a function of acid concentration, in the presence of 4-NA, in [bmim][SbF_6] at 298.1 K for sulfonic acids.

[bmim][SbF_6]	
MSA	
Concentration (M)	**ΔA**
0.0000	0
0.00306	0.107
0.00613	0.200
0.00917	0.320
0.0122	0.459
0.0158	0.469
0.0242	0.6131
0.0302	0.607
0.0359	0.700
0.0482	0.694
0.0613	0.740
0.0685	0.748
0.0876	0.847
***p*-TSA**	
-	0
0.000519	0.112
0.00105	0.194
0.00265	0.329
0.00373	0.462
0.00536	0.543
0.00725	0.625
0.00973	0.658
0.0130	0.739
0.0163	0.759
0.0223	0.770
0.0274	0.809
0.0328	0.832
TFMSA	
0.000487	0.0866
0.000619	0.190
0.000767	0.226
0.000917	0.382
0.00106	0.479
0.00121	0.644
0.00129	0.709
0.00166	0.749
0.00227	0.789
0.00290	0.837
0.00402	0.856
0.00523	0.874
0.00641	0.874
0.00761	0.909

Table S8. Absorbance variations as a function of acid concentration, in the presence of 4-NA, in [bmpyrr]NTf_2] at 298.1 K for sulfonic acids.

[bmpyrr][NTf_2]	
MSA	
Concentration (M)	**ΔA**
-	0
0.000565	0.0884
0.00136	0.182
0.00145	0.262
0.00272	0.321
0.00452	0.489
0.00565	0.522
0.0113	0.568
0.0170	0.641
0.0227	0.697
0.0339	0.699
0.0452	0.780
0.0565	0.814
***p*-TSA**	
0.00070	0.0312
0.00137	0.216
0.00144	0.136
0.00153	0.305
0.00185	0.315
0.00233	0.341
0.00271	0.413
0.00315	0.475
0.00479	0.543
0.00645	0.548
0.00763	0.611
0.00976	0.631
0.0117	0.630
0.0139	0.628
0.0164	0.624
TFMSA	
0.000229	0.0173
0.000386	0.129
0.000388	0.179
0.000499	0.299
0.000613	0.428
0.000641	0.506
0.000788	0.547
0.00108	0.629
0.00140	0.665
0.0020	0.705
0.00260	0.745
0.0036	0.781
0.00485	0.795
0.00611	0.814

Table S9. Absorbance variations as a function of acid concentration, in the presence of 4-NA, in $[bm_2im][NTf_2]$ at 298.1 K for sulfonic acids.

$[bm_2im][NTf_2]$	
MSA	
Concentration (M)	**ΔA**
-	0
0.00122	0.119
0.00306	0.223
0.00359	0.343
0.00492	0.419
0.00613	0.485
0.00919	0.573
0.0122	0.639
0.0158	0.695
0.0245	0.697
0.0292	0.803
0.0359	0.813
0.0429	0.833
0.0513	0.903
***p*-TSA**	
-	0
0.000244	0.175
0.000496	0.281
0.00100	0.323
0.00153	0.421
0.00260	0.545
0.00368	0.601
0.00532	0.739
0.00780	0.794
0.0108	0.800
0.0163	0.857
0.0218	0.866
0.0273	0.887
TFMSA	
-	0
2.04e-05	0.0470
5.67e-05	0.110
0.000121	0.264
0.000169	0.361
0.000190	0.405
0.000305	0.495
0.000397	0.642
0.000424	0.758
0.000495	0.791
0.000794	0.839
0.00131	0.871
0.00170	0.878
0.00234	0.886
0.00297	0.880

Table S10. Absorbance variations as a function of acid concentration, in the presence of 4-NA, in [bmim][NTf_2] at 298.1 K for sulfonic acids.

[bmim][NTf_2]	
MSA	
Concentration (M)	**ΔA**
-	0
0.000548	0.173
0.00112	0.289
0.00169	0.355
0.00286	0.439
0.00433	0.532
0.00583	0.635
0.00882	0.654
0.0117	0.723
0.0178	0.769
0.0238	0.752
0.0299	0.739
***p*-TSA**	
-	0
0.000105	0.103
0.000228	0.260
0.000359	0.376
0.000500	0.441
0.00142	0.567
0.00304	0.642
0.00465	0.703
0.00626	0.704
0.00960	0.746
0.0123	0.755
0.0161	0.716
TFMSA	
-	0
$1.38 \cdot 10^{-5}$	0.00610
$3.80 \cdot 10^{-5}$	0.163
$8.84 \cdot 10^{-5}$	0.261
0.000151	0.422
0.000224	0.595
0.000390	0.678
0.000760	0.727
0.00115	0.753
0.00134	0.745
0.00174	0.808
0.00223	0.779

Table S11. Observed kinetic constant values in 1,4-dioxane solution at 298.1 K for **1** →**2** rearrangement reaction in the presence of TFMSA, MSA, and *p*-TSA.

1,4-Dioxane	
TFMSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0048	0.036
0.0072	0.045
0.0096	0.046
0.012	0.051
0.014	0.054
0.017	0.057
MSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0046	$1.94 \cdot 10^{-5}$
0.0069	$2.82 \cdot 10^{-5}$
0.0092	$4.00 \cdot 10^{-5}$
0.012	$4.97 \cdot 10^{-5}$
0.014	$6.41 \cdot 10^{-5}$
0.016	$7.37 \cdot 10^{-5}$
PTSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0022	$2.88 \cdot 10^{-5}$
0.0043	$4.89 \cdot 10^{-5}$
0.0065	$1.04 \cdot 10^{-4}$
0.0087	$1.31 \cdot 10^{-4}$
0.011	$1.72 \cdot 10^{-4}$
0.013	$1.85 \cdot 10^{-4}$

Observed kinetic constants are reproducible within ± 5% from triplicate runs.

Table S12. Observed kinetic constant values in methanol solution at 298.1 K for **1 →2** rearrangement reaction in the presence of TCA, MSA, *p*-TSA, TFA and TFMSA.

Methanol	
TCA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0048	$1.33 \cdot 10^{-5}$
0.0071	$1.50 \cdot 10^{-5}$
0.0095	$1.65 \cdot 10^{-5}$
0.012	$1.93 \cdot 10^{-5}$
0.014	$2.07 \cdot 10^{-5}$
0.0167	$2.15 \cdot 10^{-5}$
MSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0049	0.00011
0.0074	0.00018
0.0098	0.00027
0.012	0.00032
0.015	0.00039
0.017	0.00047
***p*-TSA**	
Concentration (M)	k_{obs} **(s^{-1})**
0.0043	0.00013
0.0087	0.00029
0.0065	0.00020
0.011	0.00035
0.013	0.00047
0.015	0.00051
TFMSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0046	0.00014
0.0069	0.00023
0.0092	0.00031
0.011	0.00038
0.014	0.00045
0.016	0.00051
TFA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0049	$1.21 \cdot 10^{-5}$
0.0073	$1.39 \cdot 10^{-5}$
0.0097	$1.61 \cdot 10^{-5}$
0.012	$1.72 \cdot 10^{-5}$
0.014	$1.84 \cdot 10^{-5}$
0.017	$2.08 \cdot 10^{-5}$

Observed kinetic constants are reproducible within ± 5% from triplicate runs.

Table S13. Observed kinetic constant values in [bmim][BF_4] solution at 298.1 K for **1→2** rearrangement in the presence of TCA, MSA, *p*-TSA, TFA and TFMSA.

[bmim][BF_4]	
TCA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0022	$2.19 \cdot 10^{-5}$
0.0045	$3.81 \cdot 10^{-5}$
0.011	$6.97 \cdot 10^{-5}$
0.014	$8.82 \cdot 10^{-5}$
0.018	$9.96 \cdot 10^{-5}$
0.022	$1.29 \cdot 10^{-4}$
MSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0044	0.00060
0.0066	0.0012
0.0087	0.0021
0.011	0.0030
0.013	0.0039
0.015	0.0054
***p*-TSA**	
Concentration (M)	k_{obs} **(s^{-1})**
0.0043	0.000244
0.0065	0.0018
0.0087	0.0075
0.011	0.0115
0.013	0.015
0.015	0.017
TFA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0046	$6.83 \cdot 10^{-6}$
0.0070	$2.30 \cdot 10^{-5}$
0.0093	$3.70 \cdot 10^{-5}$
0.012	$5.00 \cdot 10^{-5}$
0.012	$6.83 \cdot 10^{-5}$
0.016	$8.50 \cdot 10^{-5}$

TFMSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0048	0.00086
0.0073	0.0035
0.0097	0.014
0.012	0.026
0.013	0.032
0.017	0.044

Observed kinetic constants are reproducible within ± 5% from triplicate runs.

Table S14. Observed kinetic constant values in [bmim][PF_6] solution at 298.1 K for **1→2** rearrangement in the presence of TCA, MSA, *p*-TSA and TFA.

[bmim][PF_6]	
TCA	
Concentration (M)	k_{obs} **(s^{-1})**
0.00603	$2.04 \cdot 10^{-6}$
0.00905	$4.67 \cdot 10^{-6}$
0.012	$7.82 \cdot 10^{-6}$
0.015	$1.06 \cdot 10^{-5}$
0.018	$1.67 \cdot 10^{-5}$
0.021	$2.02 \cdot 10^{-5}$
MSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0072	0.0057
0.0048	0.0037
0.0096	0.0093
0.0120	0.0121
0.0144	0.0154
0.0168	0.0192
***p*-TSA**	
Concentration (M)	k_{obs} **(s^{-1})**
0.0042	0.011
0.0064	0.017
0.0073	0.02
0.0084	0.026
0.011	0.030
0.012	0.034
TFA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0056	$3.60 \cdot 10^{-5}$
0.0084	$5.20 \cdot 10^{-5}$
0.0112	$9.55 \cdot 10^{-5}$
0.0140	$1.25 \cdot 10^{-4}$
0.0168	$1.50 \cdot 10^{-4}$
0.0196	$1.72 \cdot 10^{-4}$

Observed kinetic constants are reproducible within ± 5% from triplicate runs.

Table S15. Observed kinetic constant values in [bmim][SbF_6] solution at 298.1 K for **1→2** rearrangement in the presence of TCA, MSA, *p*-TSA and TFA.

[bmim][SbF_6]	
TCA	
Concentration (M)	k_{obs} **(s^{-1})**
0.00461	$5.92 \cdot 10^{-5}$
0.00691	$8.27 \cdot 10^{-5}$
0.00922	$9.45 \cdot 10^{-5}$
0.0115	$1.07 \cdot 10^{-4}$
0.0138	$1.28 \cdot 10^{-4}$
0.0161	$1.40 \cdot 10^{-4}$
MSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0046	$7.40 \cdot 10^{-4}$
0.0068	0.00157
0.0091	0.0022
0.011	0.0035
0.014	0.0051
0.016	0.0059
***p*-TSA**	
Concentration (M)	k_{obs} **(s^{-1})**
0.0046	0.00199
0.0068	0.00572
0.0091	0.00872
0.011	0.0121
0.014	0.0152
0.016	0.0200
TFA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0064	$1.33 \cdot 10^{-5}$
0.0096	$2.45 \cdot 10^{-5}$
0.013	$3.96 \cdot 10^{-5}$
0.016	$5.45 \cdot 10^{-5}$
0.019	$7.52 \cdot 10^{-5}$
0.022	$9.80 \cdot 10^{-5}$

Observed kinetic constants are reproducible within ± 5% from triplicate runs.

Table S16. Observed kinetic constant values in [bmpyrr][NTf_2] solution at 298.1 K for **1→2** rearrangement in the presence of TCA, MSA, *p*-TSA, and TFA.

[bmpyrr][NTf_2]	
TCA	
Concentration (M)	k_{obs} **(s^{-1})**
0.00713	$2.28 \cdot 10^{-5}$
0.00951	$3.62 \cdot 10^{-5}$
0.0119	$6.31 \cdot 10^{-5}$
0.0142	$8.42 \cdot 10^{-5}$
0.0166	$1.16 \cdot 10^{-4}$
MSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.00432	0.0071
0.00648	0.012
0.00864	0.019
0.0108	0.026
0.0133	0.033
0.0152	0.036
***p*-TSA**	
Concentration (M)	k_{obs} **(s^{-1})**
0.00443	0.0300
0.00554	0.0325
0.00664	0.0387
0.00776	0.0410
0.00886	0.0478
0.0110	0.0527
TFA	
Concentration (M)	k_{obs} **(s^{-1})**
0.00822	$8.82 \cdot 10^{-6}$
0.0109	$1.21 \cdot 10^{-5}$
0.0137	$1.91 \cdot 10^{-5}$
0.0164	$3.01 \cdot 10^{-5}$
0.0192	$3.76 \cdot 10^{-5}$

Observed kinetic constants are reproducible within ± 5% from triplicate runs.

Table S17. Observed kinetic constant values in [bmim][NTf_2] solution at 298.1 K for **1→2** rearrangement in the presence of TCA, MSA, *p*-TSA, and TFA.

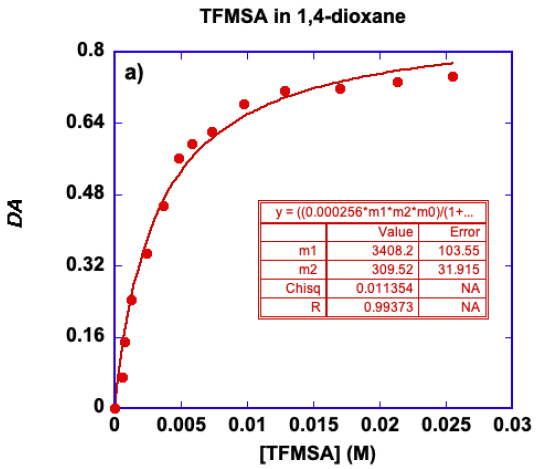
[bmim][NTf_2]	
TCA	
Concentration (M)	k_{obs} **(s^{-1})**
0.00628	$1.29 \cdot 10^{-5}$
0.00943	$1.78 \cdot 10^{-5}$
0.0126	$2.18 \cdot 10^{-5}$
0.0157	$2.03 \cdot 10^{-5}$
0.0188	$2.44 \cdot 10^{-5}$
0.0220	$3.07 \cdot 10^{-5}$
MSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0044	0.0011
0.0066	0.0025
0.0087	0.0045
0.0113	0.00736
0.0133	0.0099
0.0155	0.0133
***p*-TSA**	
Concentration (M)	k_{obs} **(s^{-1})**
0.0045	0.00608
0.0067	0.0130
0.0087	0.0185
0.011	0.0284
0.0133	0.0341
0.0152	0.0412
TFA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0091	$4.02 \cdot 10^{-6}$
0.012	$8.10 \cdot 10^{-6}$
0.015	$1.40 \cdot 10^{-5}$
0.018	$2.34 \cdot 10^{-5}$
0.021	$2.93 \cdot 10^{-5}$

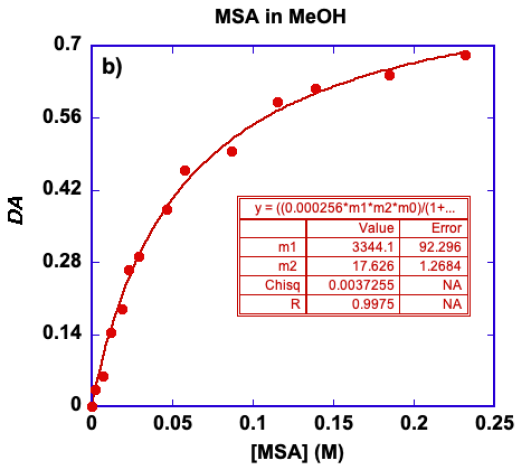
Observed kinetic constants are reproducible within ± 5% from triplicate runs.

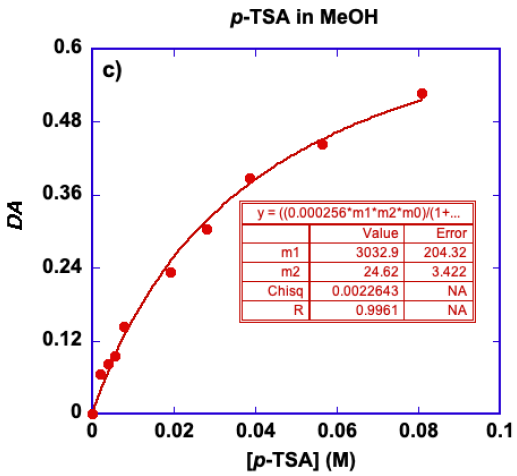
Table S18. Observed kinetic constant values in [bm_2im][NTf_2] solution at 298.1 K for **1→2** rearrangement in the presence of TCA, MSA, *p*-TSA, and TFA.

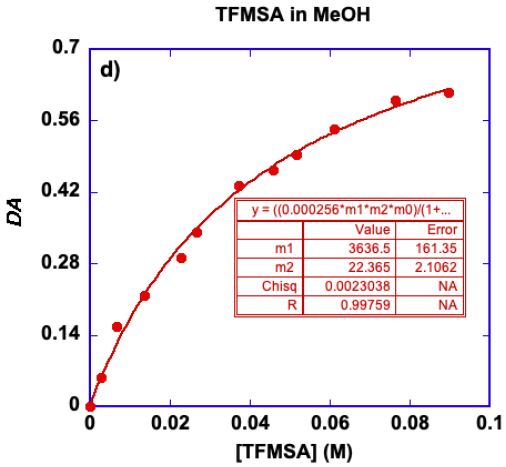
[bm_2im][NTf_2]	
TCA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0078	$1.41 \cdot 10^{-5}$
0.0103	$2.22 \cdot 10^{-5}$
0.013	$3.85 \cdot 10^{-5}$
0.015	$5.25 \cdot 10^{-5}$
0.018	$7.33 \cdot 10^{-5}$
MSA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0044	0.00382
0.0066	0.00739
0.0088	0.0118
0.011	0.0143
0.0133	0.0214
0.0155	0.0264
***p*-TSA**	
Concentration (M)	k_{obs} **(s^{-1})**
0.00457	0.0127
0.00685	0.0200
0.00913	0.0244
0.0114	0.0303
0.0137	0.0408
0.0160	0.0427
TFA	
Concentration (M)	k_{obs} **(s^{-1})**
0.0055	$8.34 \cdot 10^{-6}$
0.0082	$1.72 \cdot 10^{-5}$
0.011	$3.14 \cdot 10^{-5}$
0.014	$4.56 \cdot 10^{-5}$
0.016	$7.50 \cdot 10^{-5}$
0.019	$8.74 \cdot 10^{-5}$

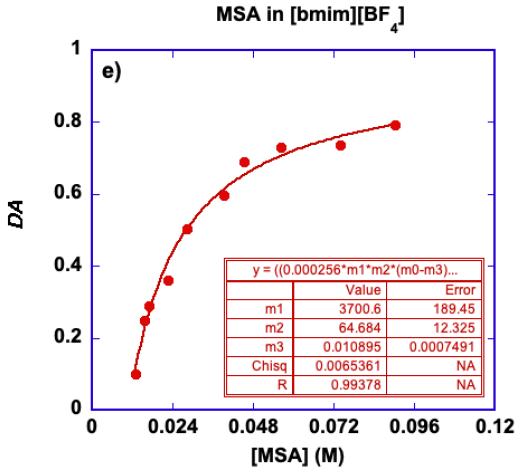
Observed kinetic constants are reproducible within ± 5% from triplicate runs.

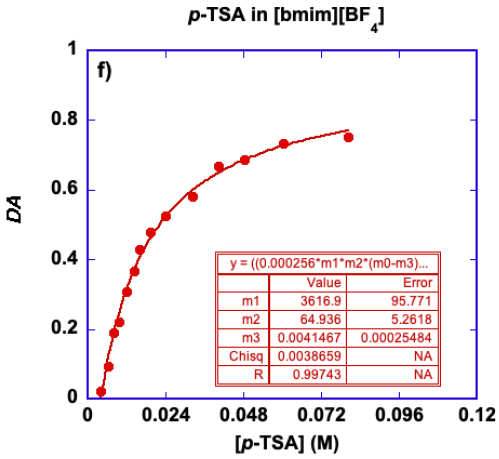

TFMSA in 1,4-dioxane
a)
DA
[TFMSA] (M)
y = ((0.000256*m1*m2*m0)/(1+...
Value Error
m1 3408.2 103.55
m2 309.52 31.915
Chisq 0.011354 NA
R 0.99373 NA

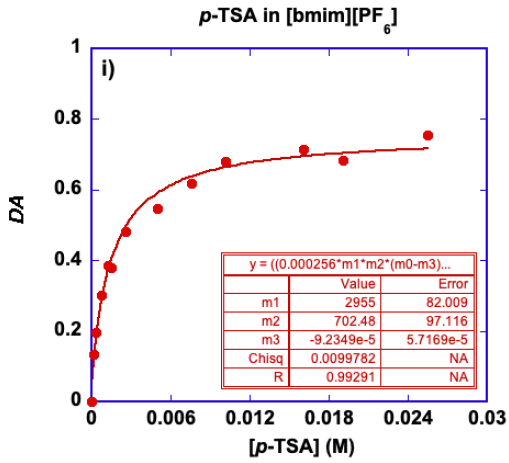

MSA in MeOH
b)
DA
[MSA] (M)
y = ((0.000256*m1*m2*m0)/(1+...
Value Error
m1 3344.1 92.296
m2 17.626 1.2684
Chisq 0.0037255 NA
R 0.9975 NA

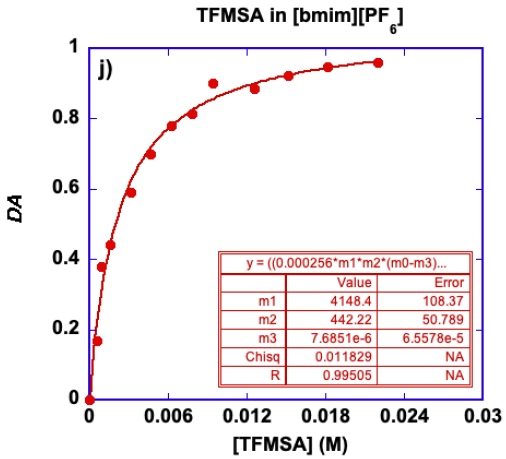

p-TSA in MeOH
c)
DA
[p-TSA] (M)
y = ((0.000256*m1*m2*m0)/(1+...
Value Error
m1 3032.9 204.32
m2 24.62 3.422
Chisq 0.0022643 NA
R 0.9961 NA

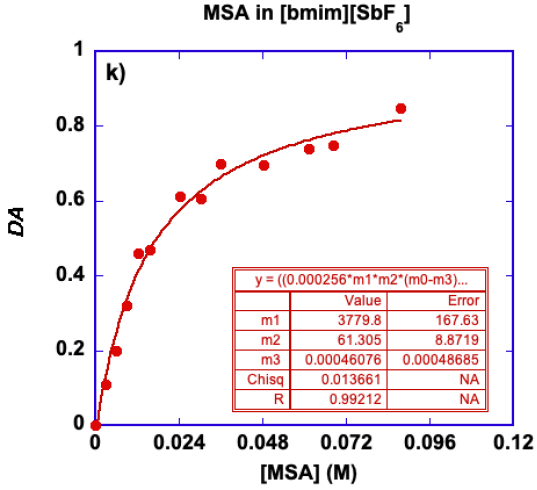

TFMSA in MeOH
d)
DA
[TFMSA] (M)
y = ((0.000256*m1*m2*m0)/(1+...
Value Error
m1 3636.5 161.35
m2 22.365 2.1062
Chisq 0.0023038 NA
R 0.99759 NA

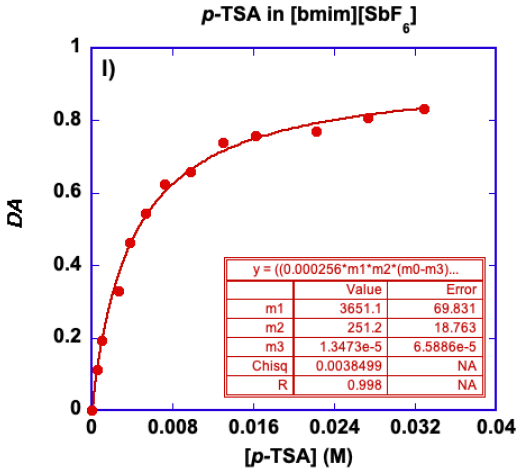

MSA in [bmim][BF4]
e)
DA
[MSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3700.6 189.45
m2 64.684 12.325
m3 0.010895 0.0007491
Chisq 0.0065361 NA
R 0.99378 NA

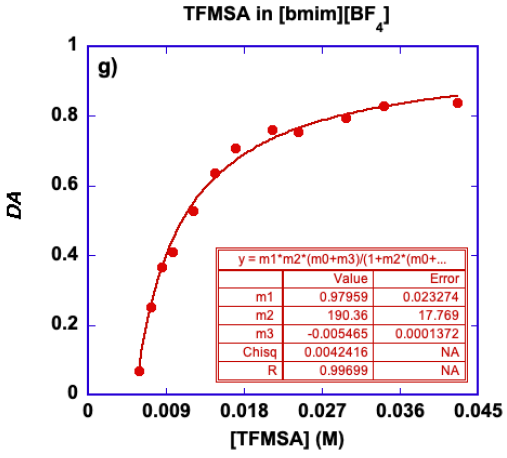

p-TSA in [bmim][BF4]
f)
DA
[p-TSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3616.9 95.771
m2 64.936 5.2618
m3 0.0041467 0.00025484
Chisq 0.0038659 NA
R 0.99743 NA

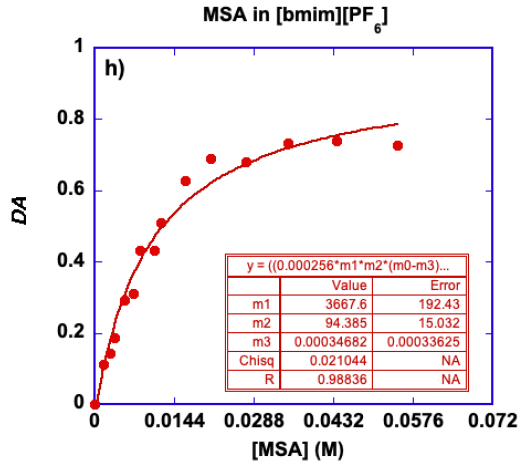

p-TSA in [bmim][PF6]
i)
DA
[p-TSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 2955 82.009
m2 702.48 97.116
m3 -9.2349e-5 5.7169e-5
Chisq 0.0099782 NA
R 0.99291 NA

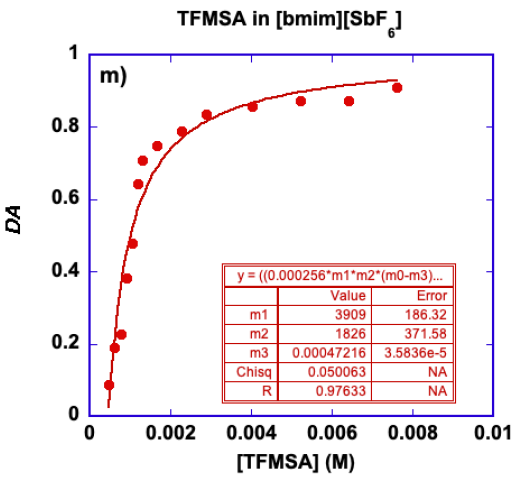

TFMSA in [bmim][PF6]
j)
DA
[TFMSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 4148.4 108.37
m2 442.22 50.789
m3 7.6851e-6 6.5578e-5
Chisq 0.011829 NA
R 0.99505 NA

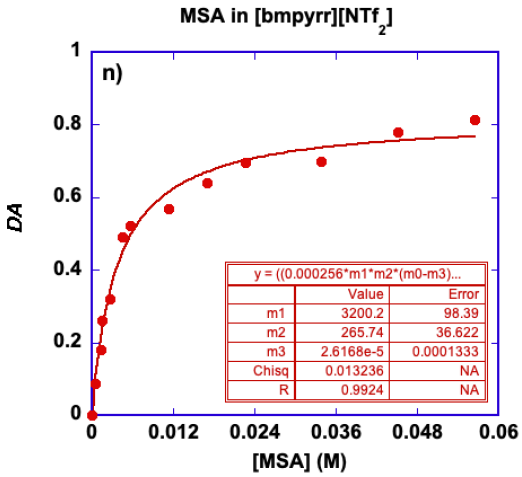

MSA in [bmim][SbF6]
k)
DA
[MSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3779.8 167.63
m2 61.305 8.8719
m3 0.00046076 0.00048685
Chisq 0.013661 NA
R 0.99212 NA

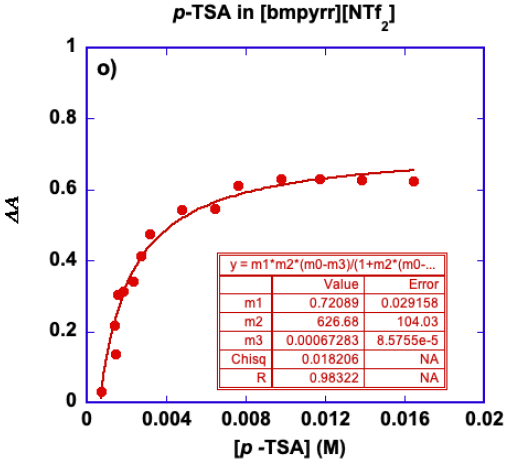

p-TSA in [bmim][SbF6]
l)
DA
[p-TSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3651.1 69.831
m2 251.2 18.763
m3 1.3473e-5 6.5886e-5
Chisq 0.0038499 NA
R 0.998 NA

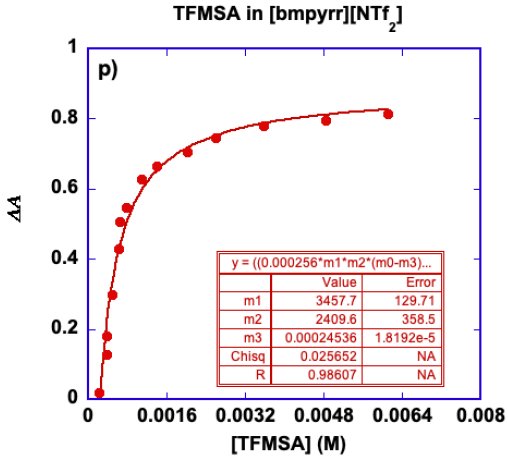

TFMSA in [bmim][BF4]
g)
DA
[TFMSA] (M)
y = m1*m2*(m0+m3)/(1+m2*(m0+...
Value Error
m1 0.97959 0.023274
m2 190.36 17.769
m3 -0.005465 0.0001372
Chisq 0.0042416 NA
R 0.99699 NA

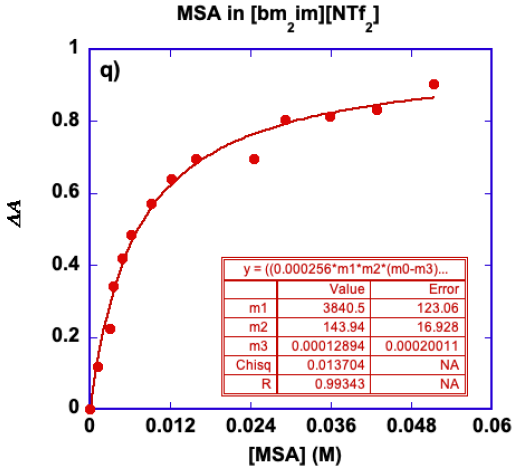

MSA in [bmim][PF6]
h)
DA
[MSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3667.6 192.43
m2 94.385 15.032
m3 0.00034682 0.00033625
Chisq 0.021044 NA
R 0.98836 NA

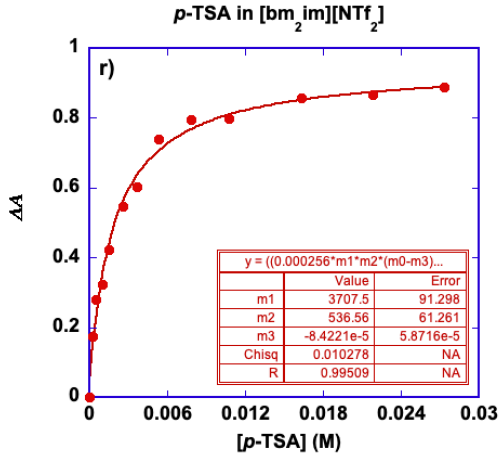

TFMSA in [bmim][SbF6]
m)
DA
[TFMSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3909 186.32
m2 1826 371.58
m3 0.00047216 3.5836e-5
Chisq 0.050063 NA
R 0.97633 NA


MSA in [bmpyrr][NTf2]
n)
DA
[MSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3200.2 98.39
m2 265.74 36.622
m3 2.6168e-5 0.0001333
Chisq 0.013236 NA
R 0.9924 NA


p-TSA in [bmpyrr][NTf2]
o)
ΔA
[p -TSA] (M)
y = m1*m2*(m0-m3)/(1+m2*(m0-...
Value Error
m1 0.72089 0.029158
m2 626.68 104.03
m3 0.00067283 8.5755e-5
Chisq 0.018206 NA
R 0.98322 NA


TFMSA in [bmpyrr][NTf2]
p)
ΔA
[TFMSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3457.7 129.71
m2 2409.6 358.5
m3 0.00024536 1.8192e-5
Chisq 0.025652 NA
R 0.98607 NA


MSA in [bm2im][NTf2]
q)
ΔA
[MSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3840.5 123.06
m2 143.94 16.928
m3 0.00012894 0.00020011
Chisq 0.013704 NA
R 0.99343 NA


p-TSA in [bm2im][NTf2]
r)
ΔA
[p-TSA] (M)
y = ((0.000256*m1*m2*(m0-m3)...
Value Error
m1 3707.5 91.298
m2 536.56 61.261
m3 -8.4221e-5 5.8716e-5
Chisq 0.010278 NA
R 0.99509 NA

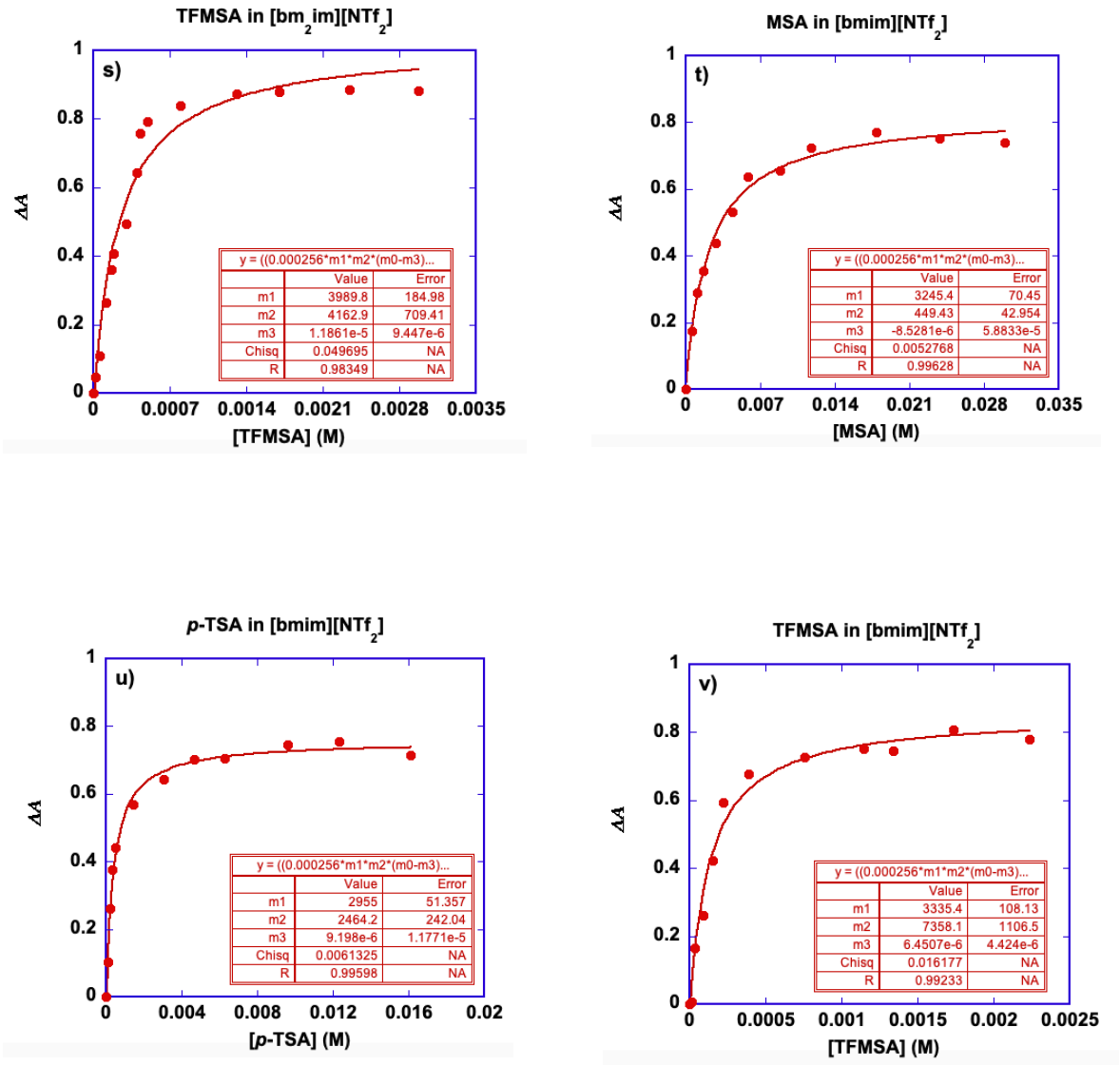
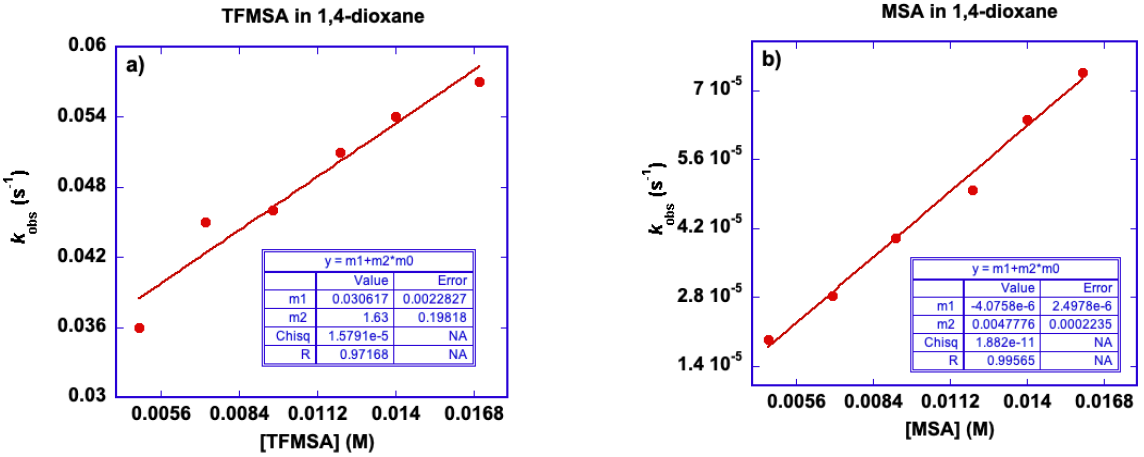
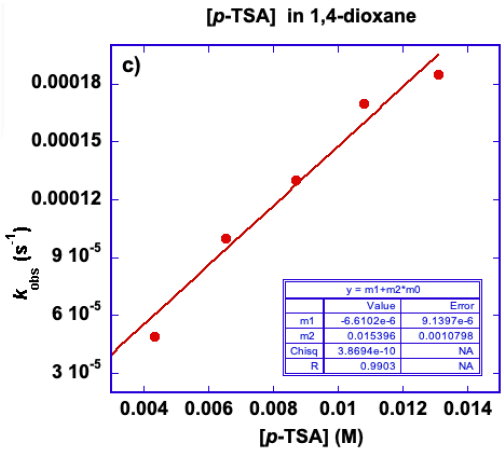
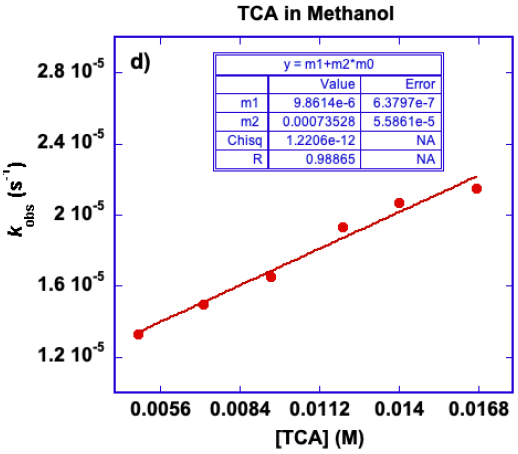
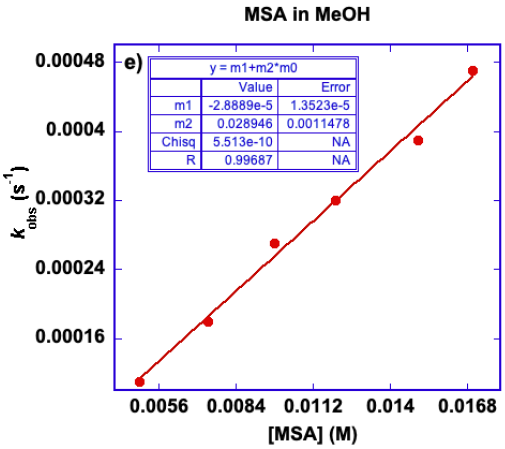


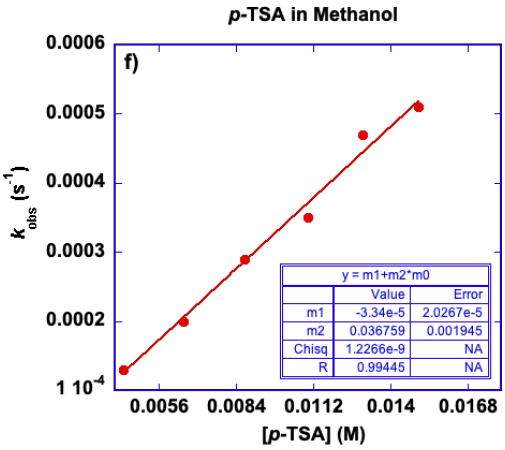
Figure S1. Plots relevant to spectroscopic measurements of $K_{ass.}$

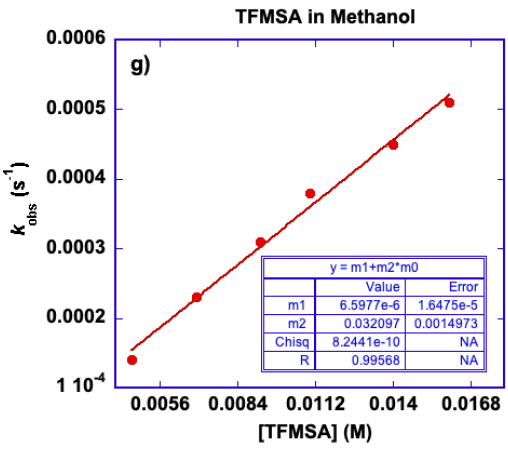


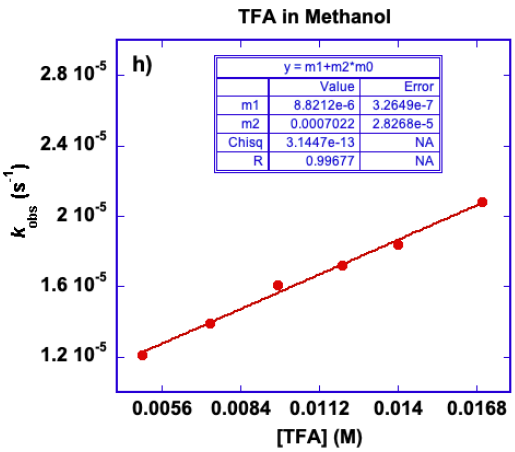

[p-TSA] in 1,4-dioxane
c)
0.00018
0.00015
0.00012
9 10-5
6 10-5
3 10-5
kobs (s-1)
0.004 0.006 0.008 0.01 0.012 0.014
[p-TSA] (M)
y = m1+m2*m0
Value Error
m1 -6.6102e-6 9.1397e-6
m2 0.015396 0.0010798
Chisq 3.8694e-10 NA
R 0.9903 NA

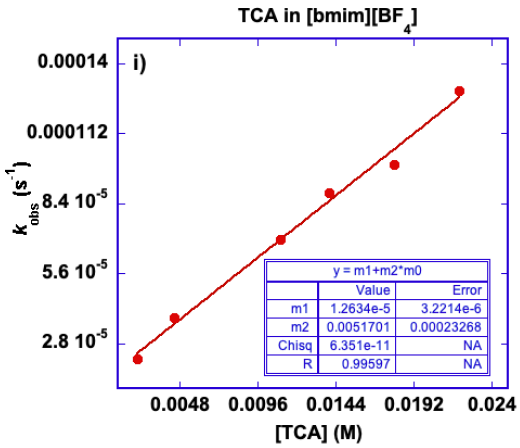

TCA in Methanol
d)
2.8 10-5
2.4 10-5
2 10-5
1.6 10-5
1.2 10-5
kobs (s-1)
0.0056 0.0084 0.0112 0.014 0.0168
[TCA] (M)
y = m1+m2*m0
Value Error
m1 9.8614e-6 6.3797e-7
m2 0.00073528 5.5861e-5
Chisq 1.2206e-12 NA
R 0.98865 NA

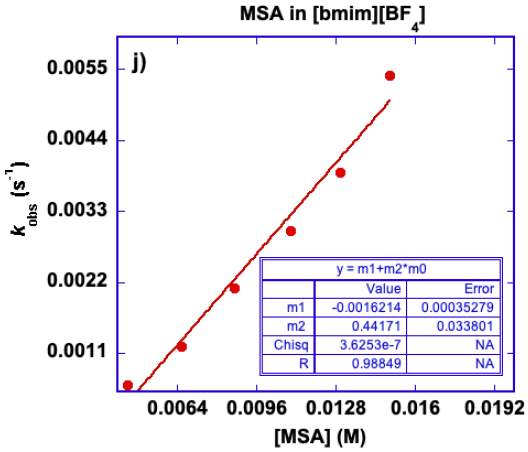

MSA in MeOH
e)
0.00048
0.0004
0.00032
0.00024
0.00016
kobs (s-1)
0.0056 0.0084 0.0112 0.014 0.0168
[MSA] (M)
y = m1+m2*m0
Value Error
m1 -2.8889e-5 1.3523e-5
m2 0.028946 0.0011478
Chisq 5.513e-10 NA
R 0.99687 NA

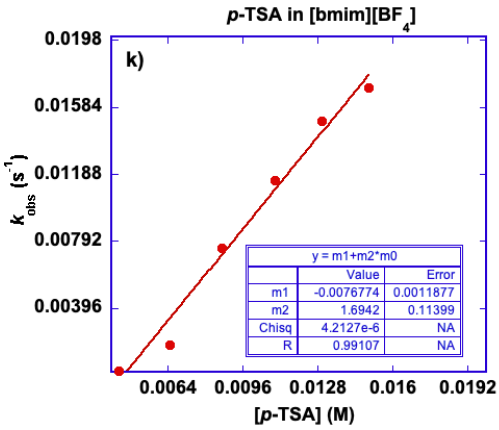

p-TSA in Methanol
f)
0.0006
0.0005
0.0004
0.0003
0.0002
1 10-4
kobs (s-1)
0.0056 0.0084 0.0112 0.014 0.0168
[p-TSA] (M)
y = m1+m2*m0
Value Error
m1 -3.34e-5 2.0267e-5
m2 0.036759 0.001945
Chisq 1.2266e-9 NA
R 0.99445 NA

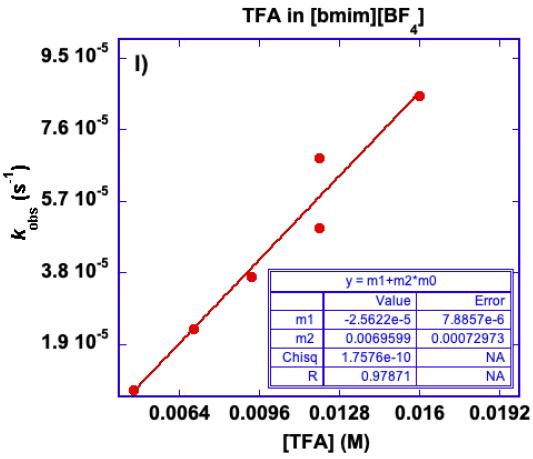

TFMSA in Methanol
g)
0.0006
0.0005
0.0004
0.0003
0.0002
1 10-4
kobs (s-1)
0.0056 0.0084 0.0112 0.014 0.0168
[TFMSA] (M)
y = m1+m2*m0
Value Error
m1 6.5977e-6 1.6475e-5
m2 0.032097 0.0014973
Chisq 8.2441e-10 NA
R 0.99568 NA

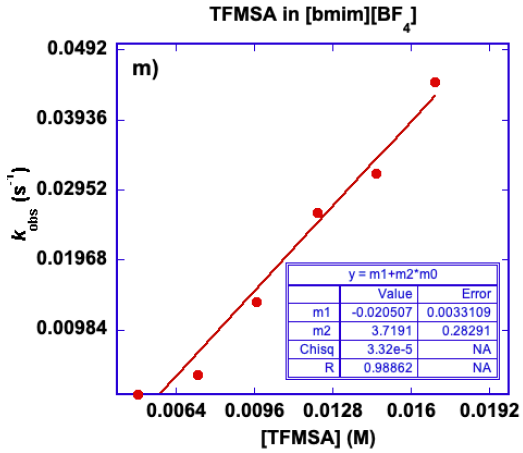

TFA in Methanol
h)
2.8 10-5
2.4 10-5
2 10-5
1.6 10-5
1.2 10-5
kobs (s-1)
0.0056 0.0084 0.0112 0.014 0.0168
[TFA] (M)
y = m1+m2*m0
Value Error
m1 8.8212e-6 3.2649e-7
m2 0.0007022 2.8268e-5
Chisq 3.1447e-13 NA
R 0.99677 NA

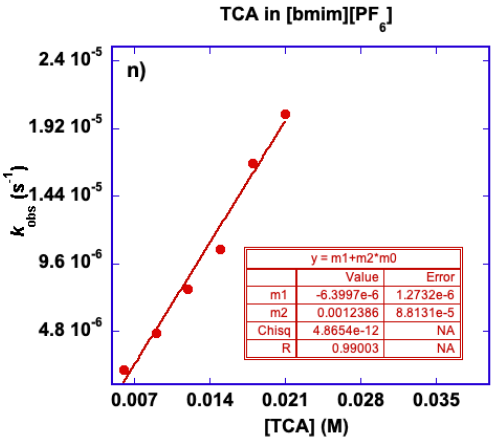

TCA in [bmim][BF4]
i)
0.00014
0.000112
8.4 10-5
5.6 10-5
2.8 10-5
kobs (s-1)
0.0048
0.0096
0.0144
0.0192
0.024
[TCA] (M)
y = m1+m2*m0
Value Error
m1 1.2634e-5 3.2214e-6
m2 0.0051701 0.00023268
Chisq 6.351e-11 NA
R 0.99597 NA

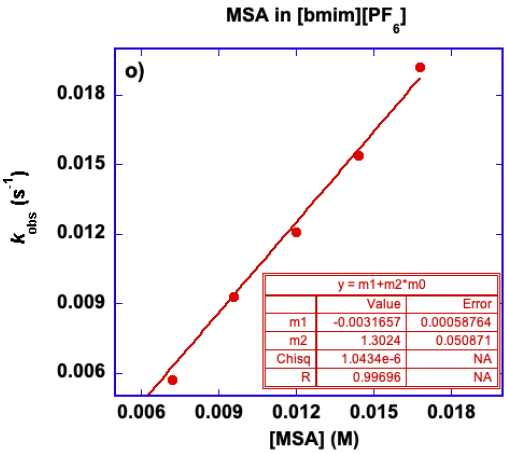

MSA in [bmim][BF4]
j)
0.0055
0.0044
0.0033
0.0022
0.0011
kobs (s-1)
0.0064
0.0096
0.0128
0.016
0.0192
[MSA] (M)
y = m1+m2*m0
Value Error
m1 -0.0016214 0.00035279
m2 0.44171 0.033801
Chisq 3.6253e-7 NA
R 0.98849 NA

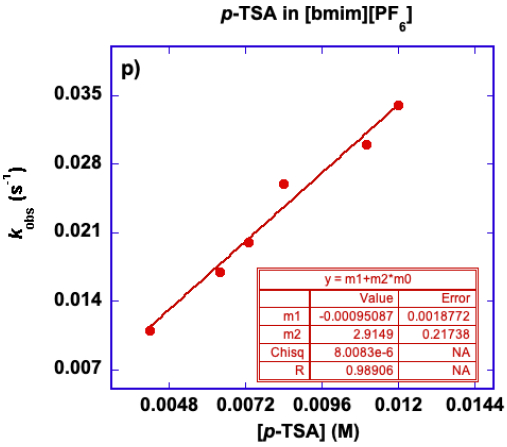

p-TSA in [bmim][BF4]
k)
0.0198
0.01584
0.01188
0.00792
0.00396
kobs (s-1)
0.0064
0.0096
0.0128
0.016
0.0192
[p-TSA] (M)
y = m1+m2*m0
Value Error
m1 -0.0076774 0.0011877
m2 1.6942 0.11399
Chisq 4.2127e-6 NA
R 0.99107 NA

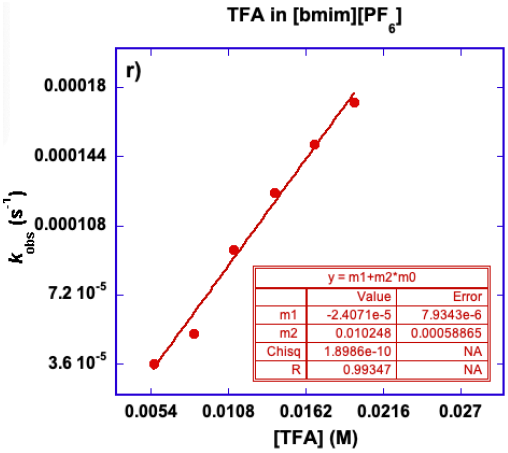

TFA in [bmim][BF4]
l)
9.5 10-5
7.6 10-5
5.7 10-5
3.8 10-5
1.9 10-5
kobs (s-1)
0.0064
0.0096
0.0128
0.016
0.0192
[TFA] (M)
y = m1+m2*m0
Value Error
m1 -2.5622e-5 7.8857e-6
m2 0.0069599 0.00072973
Chisq 1.7576e-10 NA
R 0.97871 NA

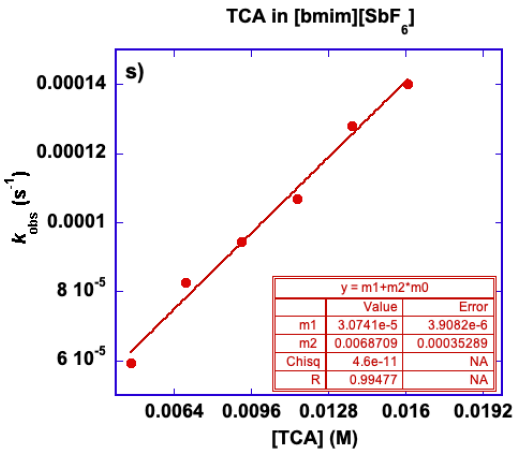

TFMSA in [bmim][BF4]
m)
0.0492
0.03936
0.02952
0.01968
0.00984
kobs (s-1)
0.0064
0.0096
0.0128
0.016
0.0192
[TFMSA] (M)
y = m1+m2*m0
Value Error
m1 -0.020507 0.0033109
m2 3.7191 0.28291
Chisq 3.32e-5 NA
R 0.98862 NA

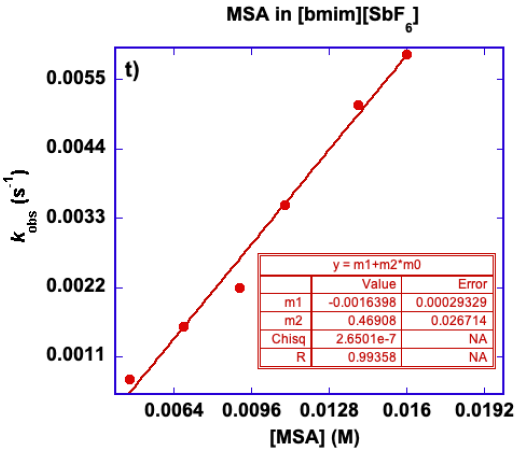

TCA in [bmim][PF6]
n)
2.4 10-5
1.92 10-5
1.44 10-5
9.6 10-6
4.8 10-6
kobs (s-1)
0.007
0.014
0.021
0.028
0.035
[TCA] (M)
y = m1+m2*m0
Value Error
m1 -6.3997e-6 1.2732e-6
m2 0.0012386 8.8131e-5
Chisq 4.8654e-12 NA
R 0.99003 NA

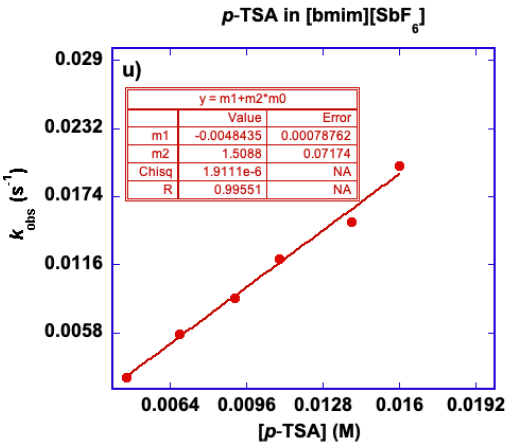

MSA in [bmim][PF6]
o)
0.018
0.015
0.012
0.009
0.006
kobs (s-1)
0.006 0.009 0.012 0.015 0.018
[MSA] (M)
y = m1+m2*m0
Value Error
m1 -0.0031657 0.00058764
m2 1.3024 0.050871
Chisq 1.0434e-6 NA
R 0.99696 NA

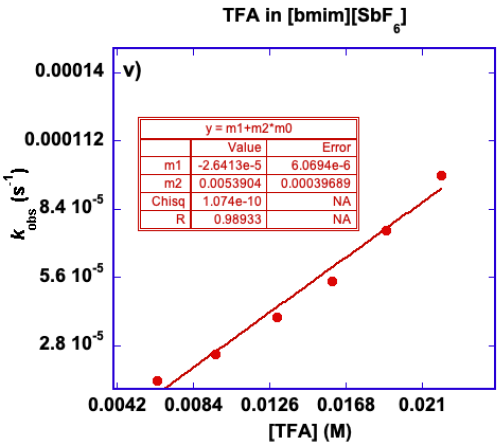

p-TSA in [bmim][PF6]
p)
0.035
0.028
0.021
0.014
0.007
kobs (s-1)
0.0048 0.0072 0.0096 0.012 0.0144
[p-TSA] (M)
y = m1+m2*m0
Value Error
m1 -0.00095087 0.0018772
m2 2.9149 0.21738
Chisq 8.0083e-6 NA
R 0.98906 NA

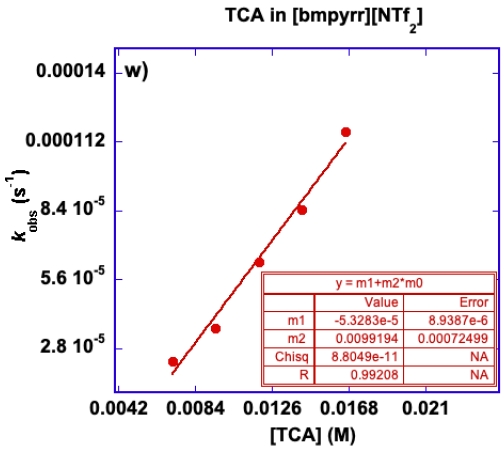

TFA in [bmim][PF6]
r)
0.00018
0.000144
0.000108
7.2 10-5
3.6 10-5
kobs (s-1)
0.0054 0.0108 0.0162 0.0216 0.027
[TFA] (M)
y = m1+m2*m0
Value Error
m1 -2.4071e-5 7.9343e-6
m2 0.010248 0.00058865
Chisq 1.8986e-10 NA
R 0.99347 NA

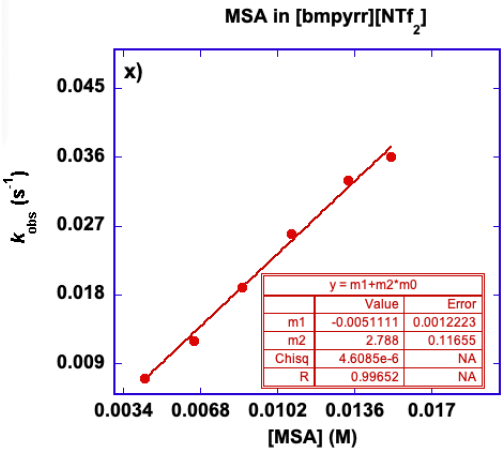

TCA in [bmim][SbF6]
s)
0.00014
0.00012
0.0001
8 10-5
6 10-5
kobs (s-1)
0.0064 0.0096 0.0128 0.016 0.0192
[TCA] (M)
y = m1+m2*m0
Value Error
m1 3.0741e-5 3.9082e-6
m2 0.0068709 0.00035289
Chisq 4.6e-11 NA
R 0.99477 NA

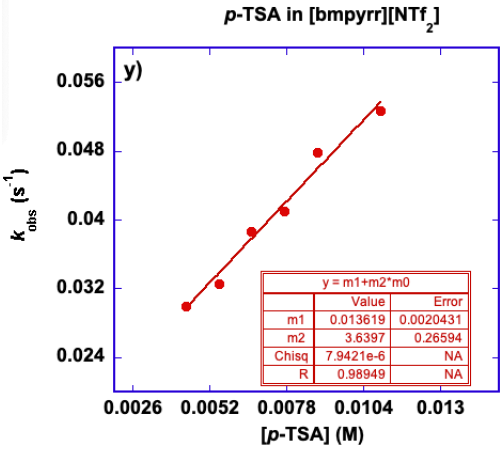

MSA in [bmim][SbF6]
t)
0.0055
0.0044
0.0033
0.0022
0.0011
kobs (s-1)
0.0064 0.0096 0.0128 0.016 0.0192
[MSA] (M)
y = m1+m2*m0
Value Error
m1 -0.0016398 0.00029329
m2 0.46908 0.026714
Chisq 2.6501e-7 NA
R 0.99358 NA

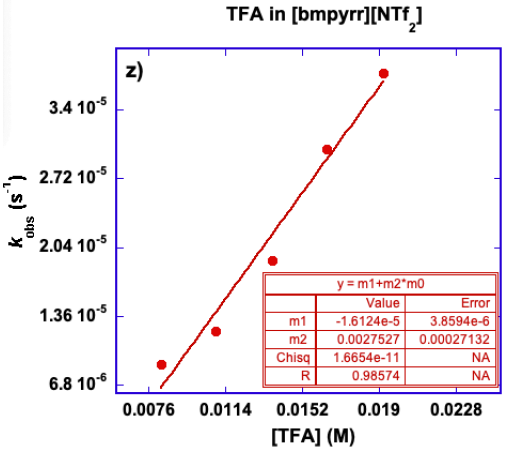

p-TSA in [bmim][SbF6]
u)
0.029
0.0232
0.0174
0.0116
0.0058
kobs (s-1)
0.0064 0.0096 0.0128 0.016 0.0192
[p-TSA] (M)
y = m1+m2*m0
Value Error
m1 -0.0048435 0.00078762
m2 1.5088 0.07174
Chisq 1.9111e-6 NA
R 0.99551 NA

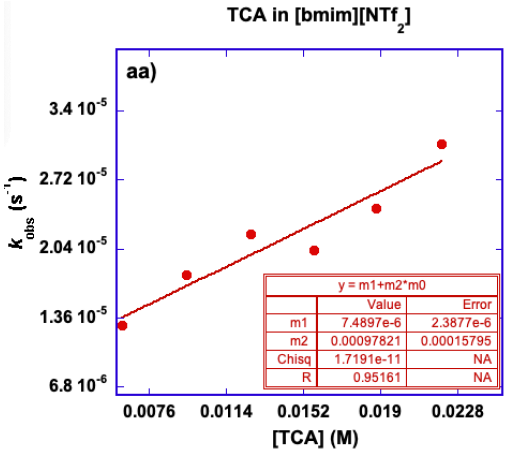

TFA in [bmim][SbF6]
v)
y = m1+m2*m0
Value Error
m1 -2.6413e-5 6.0694e-6
m2 0.0053904 0.00039689
Chisq 1.074e-10 NA
R 0.98933 NA
0.00014
0.000112
8.4 10-5
5.6 10-5
2.8 10-5
kobs (s-1)
0.0042 0.0084 0.0126 0.0168 0.021
[TFA] (M)

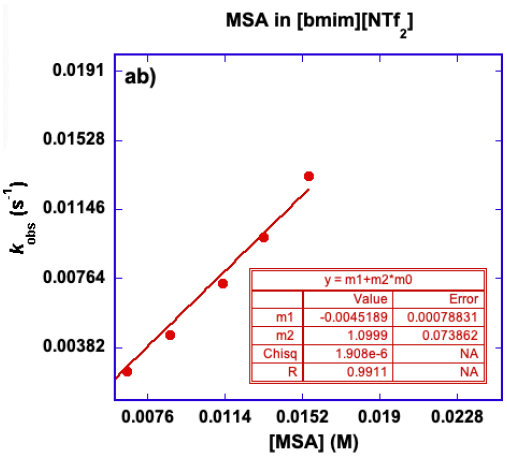

TCA in [bmpyrr][NTf2]
w)
y = m1+m2*m0
Value Error
m1 -5.3283e-5 8.9387e-6
m2 0.0099194 0.00072499
Chisq 8.8049e-11 NA
R 0.99208 NA
0.00014
0.000112
8.4 10-5
5.6 10-5
2.8 10-5
kobs (s-1)
0.0042 0.0084 0.0126 0.0168 0.021
[TCA] (M)

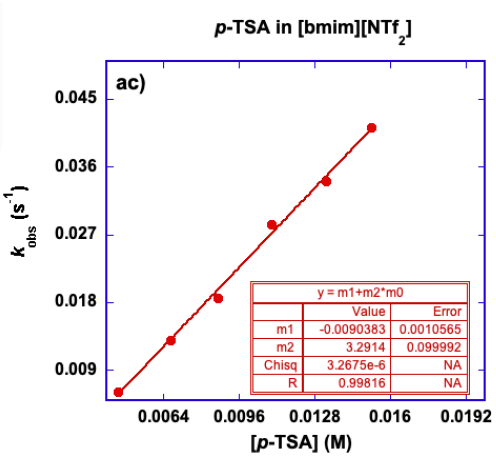

MSA in [bmpyrr][NTf2]
x)
y = m1+m2*m0
Value Error
m1 -0.0051111 0.0012223
m2 2.788 0.11655
Chisq 4.6085e-6 NA
R 0.99652 NA
0.045
0.036
0.027
0.018
0.009
kobs (s-1)
0.0034 0.0068 0.0102 0.0136 0.017
[MSA] (M)

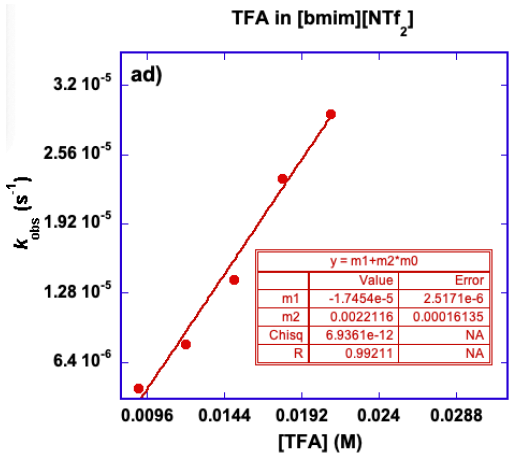

p-TSA in [bmpyrr][NTf2]
y)
y = m1+m2*m0
Value Error
m1 0.013619 0.0020431
m2 3.6397 0.26594
Chisq 7.9421e-6 NA
R 0.98949 NA
0.056
0.048
0.04
0.032
0.024
kobs (s-1)
0.0026 0.0052 0.0078 0.0104 0.013
[p-TSA] (M)

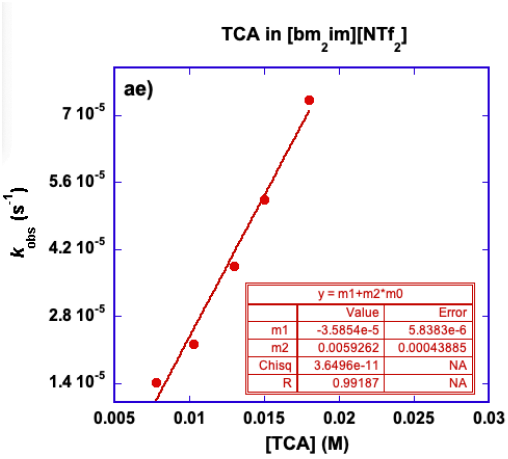

TFA in [bmpyrr][NTf2]
z)
y = m1+m2*m0
Value Error
m1 -1.6124e-5 3.8594e-6
m2 0.0027527 0.00027132
Chisq 1.6654e-11 NA
R 0.98574 NA
3.4 10-5
2.72 10-5
2.04 10-5
1.36 10-5
6.8 10-6
kobs (s-1)
0.0076 0.0114 0.0152 0.019 0.0228
[TFA] (M)

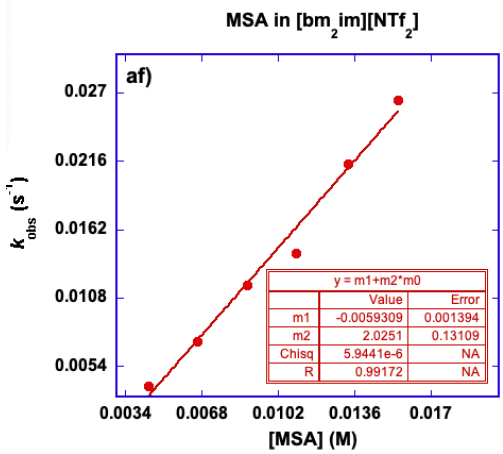

TCA in [bmim][NTf2]
aa)
y = m1+m2*m0
Value Error
m1 7.4897e-6 2.3877e-6
m2 0.00097821 0.00015795
Chisq 1.7191e-11 NA
R 0.95161 NA
3.4 10-5
2.72 10-5
2.04 10-5
1.36 10-5
6.8 10-6
kobs (s-1)
0.0076 0.0114 0.0152 0.019 0.0228
[TCA] (M)

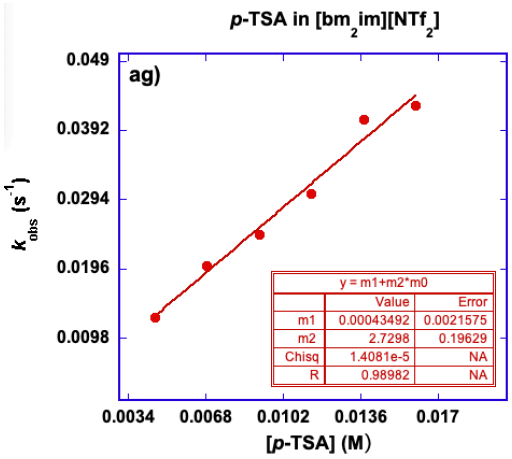

MSA in [bmim][NTf2]
ab)
0.0191
0.01528
0.01146
0.00764
0.00382
kobs (s-1)
0.0076 0.0114 0.0152 0.019 0.0228
[MSA] (M)
y = m1+m2*m0
Value Error
m1 -0.0045189 0.00078831
m2 1.0999 0.073862
Chisq 1.908e-6 NA
R 0.9911 NA


p-TSA in [bmim][NTf2]
ac)
0.045
0.036
0.027
0.018
0.009
kobs (s-1)
0.0064 0.0096 0.0128 0.016 0.0192
[p-TSA] (M)
y = m1+m2*m0
Value Error
m1 -0.0090383 0.0010565
m2 3.2914 0.099992
Chisq 3.2675e-6 NA
R 0.99816 NA


TFA in [bmim][NTf2]
ad)
3.2 10-5
2.56 10-5
1.92 10-5
1.28 10-5
6.4 10-6
kobs (s-1)
0.0096 0.0144 0.0192 0.024 0.0288
[TFA] (M)
y = m1+m2*m0
Value Error
m1 -1.7454e-5 2.5171e-6
m2 0.0022116 0.00016135
Chisq 6.9361e-12 NA
R 0.99211 NA


TCA in [bm2im][NTf2]
ae)
7 10-5
5.6 10-5
4.2 10-5
2.8 10-5
1.4 10-5
kobs (s-1)
0.005 0.01 0.015 0.02 0.025 0.03
[TCA] (M)
y = m1+m2*m0
Value Error
m1 -3.5854e-5 5.8383e-6
m2 0.0059262 0.00043885
Chisq 3.6496e-11 NA
R 0.99187 NA


MSA in [bm2im][NTf2]
af)
0.027
0.0216
0.0162
0.0108
0.0054
kobs (s-1)
0.0034 0.0068 0.0102 0.0136 0.017
[MSA] (M)
y = m1+m2*m0
Value Error
m1 -0.0059309 0.001394
m2 2.0251 0.13109
Chisq 5.9441e-6 NA
R 0.99172 NA


p-TSA in [bm2im][NTf2]
ag)
0.049
0.0392
0.0294
0.0196
0.0098
kobs (s-1)
0.0034 0.0068 0.0102 0.0136 0.017
[p-TSA] (M)
y = m1+m2*m0
Value Error
m1 0.00043492 0.0021575
m2 2.7298 0.19629
Chisq 1.4081e-5 NA
R 0.98982 NA

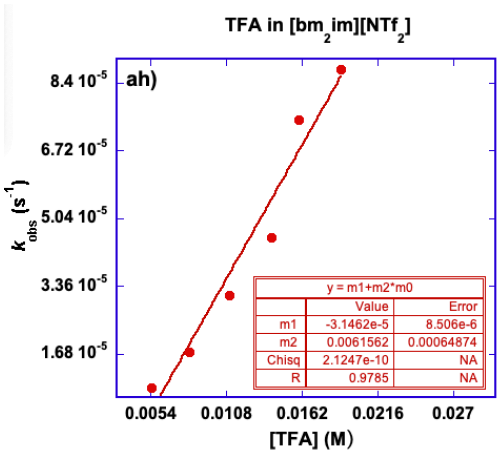


Figure S2. Plots of observed kinetic constant as a function of acid concentration.