– Electronic Supporting Information (ESI) –

Nucleophilicities and Lewis basicities of imidazoles, benzimidazoles, and benzotriazoles

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Materials

Commercially available CH_3CN (VWR, Prolabo, HPLC-gradient grade) and DMSO (>99.8%, Acros extra dry) were used as received. The benzhydrylium tetrafluoroborates Ar_2CH^+ BF_4^- were prepared as described before.[S1] All imidazoles, benzimidazoles, and benzotriazoles were purchased from commercial sources and (if necessary) purified by crystallizations or distillation prior to use.

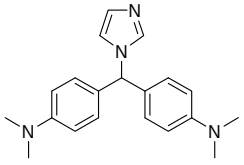
Product studies

^1H NMR chemical shifts are reported in ppm relative to the deuterated solvent as internal standard (δ_H = 7.24 for $CDCl_3$). The ^{13}C NMR chemical shifts refer to the solvent as internal standard (δ_C = 77.23 for $CDCl_3$).

Product studies with imidazoles (1)

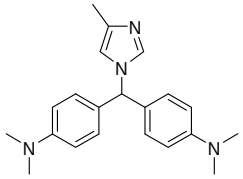
General procedure: The blue CH_3CN solution of $(dma)_2CH^+BF_4^-$ (1.0 equiv.) was added drop by drop to a solution of an appropriate imidazole **1** (10.0 eqiv.) in dry CH_3CN (10 mL) under nitrogen at room temperature. After the disappearance of the blue color of the solution, solid K_2CO_3 (1.2 equiv.) was added, and the reaction mixture was allowed to stir for a few more minutes. Then the solvent was removed in vacuum and the residue was directly transferred to the column (neutral alumina[S2]). Purification by column chromatography (EtOAc/isohexane, 1:1 as eluent) gave the desired product.

Reaction of imidazole (1a) with $(dma)_2CH^+BF_4^-$: Imidazole **1a** (200 mg, 2.94 mmol) and $(dma)_2CH^+BF_4^-$ (100 mg, 0.294 mmol) gave a light brown gummy solid (82.0 mg, 0.256 mmol, 87 %).



δ_H (300 MHz, $CDCl_3$) 2.92 (s, 12 H), 6.32 (s, 1 H), 6.65 (d, *J* 8.8 Hz, 4 H), 6.82-8.83 (m, 1 H), 6.95 (d, *J* 8.8 Hz, 4 H), 7.04 (m, 1 H) and 7.38 (s, 1 H); δ_C (75.5 MHz, $CDCl_3$) 40.7, 64.5, 112.5, 119.6, 127.6, 128.9, 129.0, 137.5 and 150.3.

Reaction of 4-methylimidazole (1e) with $(dma)_2CH^+BF_4^-$: 4-Methylimidazole **1e** (242 mg, 2.95 mmol) and $(dma)_2CH^+BF_4^-$ (100 mg, 0.294 mmol) gave a 1.0 : 0.4 mixture of two regioisomers as a yellow oil (80.8 mg, 0.242 mmol, 82 %).

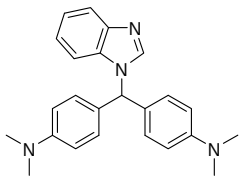


Major isomer: δ_H (300 MHz, $CDCl_3$) 2.18 (s, 3 H), 2.92 (s, 12 H), 6.24 (s, 1 H), 6.54 (s, 1 H), 6.65 (d, 4 H, *J* 9.0 Hz), 6.95 (d, 4 H, *J* 9.0 Hz) and 7.24-7.25 (m, 1 H); δ_C (75.5 MHz, $CDCl_3$) 14.0, 40.7, 64.3, 112.4, 116.0, 127.8, 129.0, 136.6, 137.9 and 150.3.

Product studies with benzimidazoles (2)

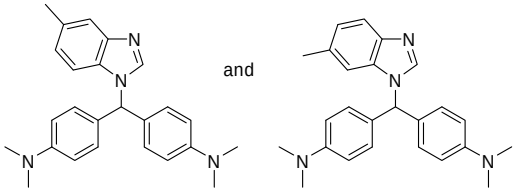
General procedure**:** The blue DMSO solution of $(dma)_2CH^+BF_4^-$ (1.0 equiv.) was added drop by drop to a solution of an appropriate benzimidazole **2** (3.0 equiv.) in dry DMSO (12 mL) under nitrogen at room temperature. After the disappearance of the blue color of the solution, solid K_2CO_3 (1.2 equiv.) was added, and reaction mixture was allowed to stir for a few more minutes. Then, the mixture was diluted with H_2O and extracted with ethyl acetate. The extract was washed several times with water and then dried ($MgSO_4$). The solvent was removed in vacuum, and the gummy residue was purified by column chromatography (neutral alumina, EtOAc/isohexane, 1:2 as eluent) to give pure product.

Reaction of benzimidazole (2a) with $(dma)_2CH^+BF_4^-$: Benzimidazole **2a** (104 mg, 0.880 mmol) and $(dma)_2CH^+BF_4^-$ (100 mg, 0.294 mmol) gave a gummy oil (82.3 mg, 0.222 mmol, 76 %).



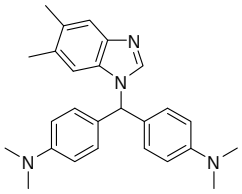
δ_H (400 MHz, $CDCl_3$) 3.00 (s, 12 H), 6.65 (s, 1 H), 6.73 (d, *J* 8.8 Hz, 4 H), 7.06 (d, *J* 8.8 Hz, 4 H), 7.20-7.33 (m, 3 H), 7.71 (s, 1 H) and 7.88 (d, *J* 8.0 Hz, 1 H); δ_C (101 MHz, $CDCl_3$) 40.6, 63.1, 111.4, 112.5, 120.2, 122.3, 122.8, 126.4, 129.1, 134.2, 143.0, 143.9 and 150.3.

Reaction of 5–methylbenzimidazole (2d) with $(dma)_2CH^+BF_4^-$: 5-Methylbenzimidazole **2d** (117 mg, 0.885 mmol) and $(dma)_2CH^+BF_4^-$ (100 mg, 0.294 mmol) gave 1 : 1 mixture of two regioisomers as a yellow gummy oil (83.1 mg, 0.216 mmol, 74 %).



δ_H (400 MHz, $CDCl_3$) 2.39/2.44 (2 s, 2 × 3 H), 2.92/2.93 (2 s, 2 × 12 H), 6.54/6.55 (2 s, 2 × 1 H = 2 H), 6.64-6.67 (m, 2 × 4 H = 8 H), 6.96-7.07 (m, 2 × 6 H = 12 H), 7.57-7.58 (m, 1 H + 2 H = 3 H), 7.68 (d, J = 8.2 Hz, 1 H); δ_C (101 MHz, $CDCl_3$) 21.7/22.0 (2 × C), 40.6 (2 × C), 62.7/63.1 (2 × C), 110.8/110.9 (2 × C), 112.5 (2 × C), 119.8/120.0 (2 × C), 123.9/124.2 (2 × C), 126.6/126.7 (2 × C), 129.1 (2 × C), 131.8/132.5/132.6/143.6 (4 × C), 142.4/142.6/143.0/144.7 (4 × C) and 150.1 (2 × C).

Reaction of 5,6-dimethylbenzimidazole (2f) with $(dma)_2CH^+BF_4^-$: 5,6-Dimethyl-benzimidazole **2f** (129 mg, 0.882 mmol) and $(dma)_2CH^+BF_4^-$ (100 mg, 0.294 mmol) gave a colorless solid (98.0 mg, 0.246 mmol, 84 %); mp. 193 °C.



δ_H (400 MHz, $CDCl_3$) 2.27 (s, 3 H), 2.33 (s, 3 H), 2.92 (s, 12 H), 6.52 (s, 1 H), 6.65 (d, J 8.8 Hz, 4 H), 6.96-6.98 (m, 5 H), 7.51 (s, 1 H) and 7.54 (s, 1 H); δ_C (101 MHz, $CDCl_3$) 20.5, 20.8, 40.6, 62.8, 111.2, 112.6, 120.3, 126.9, 129.1, 131.0, 131.8, 133.1, 142.4, 143.0 and 150.3.

Determination of equilibrium constants

Equilibrium constants were measured by UV/Vis spectroscopy in acetonitrile as follows: To solutions of the benzhydrylium tetrafluoroborates in acetonitrile small volumes of stock solutions of amines **1**–**3** were added and the decay of the absorptions was monitored. When the absorbance was constant, another portion of stock solution was added. This procedure was repeated four to eight times for each benzhydrylium salt solution.

Assuming a proportionality between the absorbances and the concentrations of the benzhydrylium ions, the equilibrium constants (*K*) can be expressed by the absorbances of the benzhydrylium ions before (A_0) and after (A) the addition of amines **1–3** using the following equation.

$$Ar_2CH^+ + NR_3 \underset{CH_3CN}{\overset{K}{\rightleftharpoons}} Ar_2CH\text{-}NR_3^+$$

$$K = \frac{[Ar_2CH\text{-}NR_3^+]}{[Ar_2CH^+]\,[NR_3]} = \frac{A_0 - A}{A\,[NR_3]}$$

Where $[NR_3] = [NR_3]_0 - [Ar_2CH\text{-}NR_3^+]$

The temperature of the solutions during all equilibrium studies was kept constant at 20 °C using a circulating bath thermostat.

Equilibrium constant for the reaction of 1-methylimidazole (**1b**) and $(lil)_2CH^+BF_4^-$
ε [$(lil)_2CH^+BF_4^-$ at 631 nm] = 1.32×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**1b**]$_0$ (mol L^{-1})	A	[$(lil)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.767	1.164×10^{-5}	
1	3.582×10^{-4}	0.701	1.064×10^{-5}	2.59×10^2
2	1.424×10^{-3}	0.563	8.536×10^{-6}	2.49×10^2
3	2.478×10^{-3}	0.471	7.154×10^{-6}	2.45×10^2
4	3.520×10^{-3}	0.405	6.150×10^{-6}	2.44×10^2
5	4.550×10^{-3}	0.355	5.390×10^{-6}	2.44×10^2
6	5.568×10^{-3}	0.316	4.796×10^{-6}	2.43×10^2
7	6.574×10^{-3}	0.284	4.315×10^{-6}	2.44×10^2
8	7.569×10^{-3}	0.258	3.921×10^{-6}	2.44×10^2
0	0	0.683	1.037×10^{-5}	
1	1.078×10^{-3}	0.536	8.126×10^{-6}	2.49×10^2
2	2.495×10^{-3}	0.419	6.355×10^{-6}	2.44×10^2
3	3.891×10^{-3}	0.343	5.208×10^{-6}	2.44×10^2
4	5.265×10^{-3}	0.291	4.411×10^{-6}	2.44×10^2
5	6.618×10^{-3}	0.252	3.830×10^{-6}	2.43×10^2

6	7.951×10^{-3}	0.223	3.378×10^{-6}	2.44×10^{2}
0	0	0.700	1.062×10^{-5}	
1	1.479×10^{-3}	0.511	7.754×10^{-6}	2.43×10^{2}
2	2.934×10^{-3}	0.404	6.126×10^{-6}	2.41×10^{2}
3	4.365×10^{-3}	0.334	5.067×10^{-6}	2.40×10^{2}
4	5.774×10^{-3}	0.284	4.316×10^{-6}	2.40×10^{2}
5	7.161×10^{-3}	0.248	3.756×10^{-6}	2.40×10^{2}
6	8.527×10^{-3}	0.220	3.335×10^{-6}	2.39×10^{2}

K_{av}(20 °C) = 2.44×10^{2} L mol^{-1}

Equilibrium constant for the reaction of 1-methylimidazole (**1b**) and $(jul)_2CH^+BF_4^-$
ε [$(jul)_2CH^+BF_4^-$ at 635 nm] = 1.73×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**1b**]$_0$ (mol L^{-1})	A	[$(jul)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.606	7.022×10^{-6}	
1	1.211×10^{-3}	0.465	5.390×10^{-6}	2.40×10^{2}
2	2.399×10^{-3}	0.378	4.373×10^{-6}	2.40×10^{2}
3	3.564×10^{-3}	0.317	3.666×10^{-6}	2.42×10^{2}
4	4.708×10^{-3}	0.274	3.170×10^{-6}	2.41×10^{2}
5	5.831×10^{-3}	0.240	2.774×10^{-6}	2.43×10^{2}
6	6.932×10^{-3}	0.214	2.472×10^{-6}	2.43×10^{2}
0	0	0.617	7.150×10^{-6}	
1	1.241×10^{-3}	0.470	5.447×10^{-6}	2.42×10^{2}
2	2.459×10^{-3}	0.379	4.390×10^{-6}	2.43×10^{2}
3	3.652×10^{-3}	0.319	3.690×10^{-6}	2.42×10^{2}
4	4.823×10^{-3}	0.274	3.176×10^{-6}	2.42×10^{2}
5	5.971×10^{-3}	0.240	2.782×10^{-6}	2.43×10^{2}
6	7.098×10^{-3}	0.214	2.477×10^{-6}	2.43×10^{2}

K_{av}(20 °C) = 2.42×10^{2} L mol^{-1}

Equilibrium constant for the reaction of 1-methylimidazole (**1b**) and $(ind)_2CH^+BF_4^-$
ε [$(ind)_2CH^+BF_4^-$ at 616 nm] = 1.29×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**1b**]$_0$ (mol L^{-1})	A	[$(ind)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.578	8.981×10^{-6}	
1	1.766×10^{-4}	0.299	4.651×10^{-6}	5.39×10^{3}
2	3.529×10^{-4}	0.199	3.096×10^{-6}	5.46×10^{3}
3	5.289×10^{-4}	0.148	2.302×10^{-6}	5.53×10^{3}
4	7.045×10^{-4}	0.119	1.848×10^{-6}	5.51×10^{3}
5	8.798×10^{-4}	0.099	1.542×10^{-6}	5.50×10^{3}
6	1.055×10^{-4}	0.085	1.316×10^{-6}	5.52×10^{3}
0	0	0.596	9.268×10^{-6}	
1	1.793×10^{-4}	0.301	4.671×10^{-6}	5.62×10^{3}
2	3.582×10^{-4}	0.201	3.130×10^{-6}	5.55×10^{3}
3	5.368×10^{-4}	0.150	2.335×10^{-6}	5.58×10^{3}
4	7.150×10^{-4}	0.121	1.875×10^{-6}	5.54×10^{3}
5	8.929×10^{-4}	0.100	1.552×10^{-6}	5.58×10^{3}

0	0	0.601	9.336×10^{-6}	
1	1.829×10^{-4}	0.300	4.666×10^{-6}	5.60×10^{3}
2	3.655×10^{-4}	0.198	3.071×10^{-6}	5.66×10^{3}
3	5.477×10^{-4}	0.149	2.318×10^{-6}	5.58×10^{3}
4	7.295×10^{-4}	0.118	1.831×10^{-6}	5.65×10^{3}
5	9.110×10^{-4}	0.098	1.523×10^{-6}	5.64×10^{3}
6	1.092×10^{-3}	0.084	1.307×10^{-6}	5.63×10^{3}

K_{av}(20 °C) = 5.56×10^{3} L mol^{-1}

Equilibrium constant for the reaction of 1-methylimidazole and $(thq)_2CH^+BF_4^-$
ε [$(thq)_2CH^+BF_4^-$ at 620 nm] = 1.01×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**1b**]$_0$ (mol L^{-1})	A	[$(thq)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.373	7.417×10^{-6}	
1	1.205×10^{-4}	0.185	3.684×10^{-6}	8.66×10^{3}
2	2.409×10^{-4}	0.122	2.421×10^{-6}	8.72×10^{3}
3	3.609×10^{-4}	0.091	1.812×10^{-6}	8.67×10^{3}
4	4.808×10^{-4}	0.073	1.443×10^{-6}	8.68×10^{3}
5	6.004×10^{-4}	0.061	1.203×10^{-6}	8.64×10^{3}
0	0	0.366	7.268×10^{-6}	
1	1.242×10^{-4}	0.177	3.528×10^{-6}	8.78×10^{3}
2	2.481×10^{-4}	0.115	2.282×10^{-6}	8.96×10^{3}
3	3.718×10^{-4}	0.086	1.715×10^{-6}	8.81×10^{3}
4	4.952×10^{-4}	0.068	1.355×10^{-6}	8.87×10^{3}
5	6.184×10^{-4}	0.057	1.141×10^{-6}	8.72×10^{3}
0	0	0.349	6.932×10^{-6}	
1	1.194×10^{-4}	0.175	3.473×10^{-6}	8.58×10^{3}
2	2.385×10^{-4}	0.115	2.280×10^{-6}	8.70×10^{3}
3	3.575×10^{-4}	0.086	1.706×10^{-6}	8.67×10^{3}
4	4.762×10^{-4}	0.069	1.373×10^{-6}	8.56×10^{3}
5	5.946×10^{-4}	0.058	1.160×10^{-6}	8.40×10^{3}

K_{av}(20 °C) = 8.69×10^{3} L mol^{-1}

Equilibrium constant for the reaction of 1-phenylimidazole (**1c**) and $(ind)_2CH^+BF_4^-$
ε [$(ind)_2CH^+BF_4^-$ at 616 nm] = 1.29×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**1c**]$_0$ (mol L^{-1})	A	[$(ind)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.660	1.025×10^{-5}	
1	3.105×10^{-3}	0.504	7.831×10^{-6}	9.07×10^{1}
2	6.081×10^{-3}	0.409	6.361×10^{-6}	8.96×10^{1}
3	8.937×10^{-3}	0.344	5.340×10^{-6}	8.99×10^{1}
4	1.168×10^{-2}	0.296	4.601×10^{-6}	9.00×10^{1}
5	1.432×10^{-2}	0.261	4.058×10^{-6}	8.95×10^{1}
0	0	0.617	9.585×10^{-6}	
1	2.917×10^{-3}	0.475	7.378×10^{-6}	9.38×10^{1}
2	5.720×10^{-3}	0.390	6.057×10^{-6}	9.11×10^{1}
3	8.417×10^{-3}	0.329	5.113×10^{-6}	9.12×10^{1}

4	1.101×10^{-2}	0.287	4.462×10^{-6}	8.97×10^{1}
5	1.351×10^{-2}	0.253	3.930×10^{-6}	8.99×10^{1}
0	0	0.639	9.931×10^{-6}	
1	1.801×10^{-3}	0.541	8.405×10^{-6}	9.28×10^{1}
2	4.134×10^{-3}	0.451	7.014×10^{-6}	9.10×10^{1}
3	6.394×10^{-3}	0.386	6.002×10^{-6}	9.12×10^{1}
4	8.583×10^{-3}	0.338	5.252×10^{-6}	9.10×10^{1}
5	1.123×10^{-2}	0.293	4.554×10^{-6}	9.04×10^{1}

K_{av}(20 °C) = 9.08×10^{1} L mol^{-1}

Equilibrium constant for the reaction of 1-phenylimidazole (**1c**) and $(thq)_2CH^+BF_4^-$
ε [$(thq)_2CH^+BF_4^-$ at 620 nm] = 1.01×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**1c**]$_0$ (mol L^{-1})	A	[$(thq)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.541	1.076×10^{-5}	
1	1.346×10^{-3}	0.426	8.472×10^{-6}	1.91×10^{2}
2	2.927×10^{-3}	0.344	6.833×10^{-6}	1.85×10^{2}
3	4.470×10^{-3}	0.288	5.730×10^{-6}	1.83×10^{2}
4	6.226×10^{-3}	0.242	4.812×10^{-6}	1.82×10^{2}
5	7.935×10^{-3}	0.209	4.150×10^{-6}	1.82×10^{2}
0	0	0.517	1.028×10^{-5}	
1	1.604×10^{-3}	0.393	7.810×10^{-6}	1.88×10^{2}
2	3.171×10^{-3}	0.320	6.361×10^{-6}	1.82×10^{2}
3	4.701×10^{-3}	0.269	5.356×10^{-6}	1.81×10^{2}
4	6.686×10^{-3}	0.222	4.421×10^{-6}	1.81×10^{2}
5	8.613×10^{-3}	0.189	3.764×10^{-6}	1.81×10^{2}
0	0	0.495	9.835×10^{-6}	
1	1.588×10^{-3}	0.378	7.522×10^{-6}	1.84×10^{2}
2	3.139×10^{-3}	0.308	6.127×10^{-6}	1.81×10^{2}
3	4.655×10^{-3}	0.260	5.172×10^{-6}	1.80×10^{2}
4	6.622×10^{-3}	0.215	4.273×10^{-6}	1.80×10^{2}
5	8.531×10^{-3}	0.182	3.627×10^{-6}	1.81×10^{2}

K_{av}(20 °C) = 1.83×10^{2} L mol^{-1}

Equilibrium constant for the reaction of 1–phenylimidazole (**1c**) and $(pyr)_2CH^+BF_4^-$
ε [$(pyr)_2CH^+BF_4^-$ at 612 nm] = 1.39×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**1Ph Imi**]$_0$ (mol L^{-1})	A	[$(pyr)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.516	7.422×10^{-6}	
1	1.213×10^{-3}	0.323	4.653×10^{-6}	4.81×10^{2}
2	2.405×10^{-3}	0.238	3.423×10^{-6}	4.71×10^{2}
3	3.578×10^{-3}	0.189	2.716×10^{-6}	4.66×10^{2}
4	4.731×10^{-3}	0.157	2.255×10^{-6}	4.62×10^{2}
5	5.865×10^{-3}	0.133	1.915×10^{-6}	4.63×10^{2}
0	0	0.527	7.585×10^{-6}	
1	1.831×10^{-3}	0.282	4.057×10^{-6}	4.63×10^{2}
2	3.026×10^{-3}	0.216	3.102×10^{-6}	4.61×10^{2}

3	4.201×10^{-3}	0.176	2.527×10^{-6}	4.56×10^{2}
4	5.357×10^{-3}	0.147	2.116×10^{-6}	4.58×10^{2}
0	0	0.521	7.496×10^{-6}	
1	9.322×10^{-5}	0.494	7.108×10^{-6}	5.15×10^{2}
2	3.956×10^{-4}	0.425	6.110×10^{-6}	4.91×10^{2}
3	6.857×10^{-4}	0.373	5.373×10^{-6}	4.83×10^{2}
4	9.643×10^{-4}	0.333	4.798×10^{-6}	4.78×10^{2}
5	1.232×10^{-3}	0.302	4.342×10^{-6}	4.73×10^{2}
6	1.490×10^{-3}	0.276	3.965×10^{-6}	4.70×10^{2}
7	1.737×10^{-3}	0.253	3.644×10^{-6}	4.69×10^{2}

K_{av}(20 °C) = 4.72×10^{2} L mol^{-1}

Equilibrium constant for the reaction of 1-phenylimidazole and $(dma)_2CH^+BF_4^-$
ε [$(dma)_2CH^+BF_4^-$ at 605 nm] = 1.46×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**1c**]$_0$ (mol L^{-1})	A	[$(dma)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.573	7.828×10^{-6}	
1	6.084×10^{-5}	0.443	6.046×10^{-6}	4.90×10^{3}
2	1.212×10^{-4}	0.357	4.875×10^{-6}	5.01×10^{3}
3	2.108×10^{-4}	0.276	3.774×10^{-6}	5.05×10^{3}
4	2.992×10^{-4}	0.225	3.079×10^{-6}	5.06×10^{3}
5	3.867×10^{-4}	0.190	2.597×10^{-6}	5.07×10^{3}
0	0	0.572	7.811×10^{-6}	
1	6.084×10^{-5}	0.439	5.998×10^{-6}	5.03×10^{3}
2	1.212×10^{-4}	0.356	4.858×10^{-6}	5.03×10^{3}
3	2.108×10^{-4}	0.276	3.766×10^{-6}	5.05×10^{3}
4	2.992×10^{-4}	0.223	3.051×10^{-6}	5.12×10^{3}
5	3.867×10^{-4}	0.188	2.571×10^{-6}	5.13×10^{3}
0	0	0.788	1.077×10^{-5}	
1	3.176×10^{-5}	0.689	9.418×10^{-6}	4.64×10^{3}
2	9.486×10^{-5}	0.541	7.385×10^{-6}	4.91×10^{3}
3	1.574×10^{-4}	0.444	6.064×10^{-6}	4.95×10^{3}
4	2.195×10^{-4}	0.378	5.161×10^{-6}	4.93×10^{3}
5	2.810×10^{-4}	0.326	4.453×10^{-6}	5.00×10^{3}
6	3.419×10^{-4}	0.288	3.937×10^{-6}	4.99×10^{3}

K_{av}(20 °C) = 4.99×10^{3} L mol^{-1}

Equilibrium constant for the reaction of 1-methylbenzimidazole (**2b**) and $(ind)_2CH^+BF_4^-$
ε [$(ind)_2CH^+BF_4^-$ at 616 nm] = 1.29×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**2b**]$_0$ (mol L^{-1})	A	[$(ind)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.761	1.183×10^{-5}	
1	7.482×10^{-4}	0.649	1.009×10^{-5}	2.25×10^{2}
2	2.227×10^{-3}	0.526	8.172×10^{-6}	1.94×10^{2}
3	4.401×10^{-3}	0.411	6.390×10^{-6}	1.84×10^{2}
4	6.525×10^{-3}	0.338	5.257×10^{-6}	1.80×10^{2}
5	8.600×10^{-3}	0.290	4.506×10^{-6}	1.75×10^{2}

6	1.063×10^{-2}	0.253	3.936×10^{-6}	1.73×10^{2}
0	0	0.777	1.207×10^{-5}	
1	1.850×10^{-3}	0.559	8.692×10^{-6}	2.03×10^{2}
2	3.664×10^{-3}	0.451	7.004×10^{-6}	1.89×10^{2}
3	5.442×10^{-3}	0.378	5.866×10^{-6}	1.84×10^{2}
4	7.186×10^{-3}	0.326	5.061×10^{-6}	1.80×10^{2}
5	8.898×10^{-3}	0.287	4.457×10^{-6}	1.78×10^{2}
6	1.058×10^{-2}	0.257	3.988×10^{-6}	1.76×10^{2}
0	0	0.793	1.233×10^{-5}	
1	1.869×10^{-3}	0.571	8.869×10^{-6}	2.02×10^{2}
2	3.700×10^{-3}	0.457	7.106×10^{-6}	1.90×10^{2}
3	5.496×10^{-3}	0.383	5.957×10^{-6}	1.84×10^{2}
4	7.257×10^{-3}	0.331	5.146×10^{-6}	1.80×10^{2}
5	8.984×10^{-3}	0.292	4.534×10^{-6}	1.77×10^{2}
6	1.068×10^{-2}	0.261	4.052×10^{-6}	1.75×10^{2}

K_{av}(20 °C) = 1.86×10^{2} L mol^{-1}

Equilibrium constant for the reaction of 1-methylbenzimidazole (**2b**) and $(thq)_2CH^+BF_4^-$
ε [$(thq)_2CH^+BF_4^-$ at 620 nm] = 1.01×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**2b**]$_0$ (mol L^{-1})	A	[$(thq)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.645	1.283×10^{-5}	
1	1.364×10^{-3}	0.463	9.203×10^{-6}	2.81×10^{2}
2	2.707×10^{-3}	0.368	7.312×10^{-6}	2.69×10^{2}
3	4.028×10^{-3}	0.308	6.125×10^{-6}	2.60×10^{2}
4	5.329×10^{-3}	0.265	5.268×10^{-6}	2.55×10^{2}
5	6.610×10^{-3}	0.233	4.631×10^{-6}	2.52×10^{2}
6	7.871×10^{-3}	0.208	4.133×10^{-6}	2.49×10^{2}
0	0	0.584	1.160×10^{-5}	
1	1.330×10^{-3}	0.423	8.407×10^{-6}	2.78×10^{2}
2	2.640×10^{-3}	0.338	6.721×10^{-6}	2.65×10^{2}
3	3.930×10^{-3}	0.283	5.629×10^{-6}	2.58×10^{2}
4	5.200×10^{-3}	0.244	4.857×10^{-6}	2.53×10^{2}
5	6.451×10^{-3}	0.215	4.275×10^{-6}	2.50×10^{2}
6	7.683×10^{-3}	0.193	3.833×10^{-6}	2.46×10^{2}
0	0	0.606	1.205×10^{-5}	
1	1.385×10^{-3}	0.433	8.615×10^{-6}	2.81×10^{2}
2	2.749×10^{-3}	0.344	6.845×10^{-6}	2.67×10^{2}
3	4.090×10^{-3}	0.286	5.693×10^{-6}	2.61×10^{2}
4	5.410×10^{-3}	0.246	4.896×10^{-6}	2.56×10^{2}
5	6.709×10^{-3}	0.216	4.296×10^{-6}	2.53×10^{2}
6	7.988×10^{-3}	0.193	3.846×10^{-6}	2.49×10^{2}

K_{av}(20 °C) = 2.60×10^{2} L mol^{-1}

Equilibrium constant for the reaction of 1-methylbenzimidazole (**2b**) and $(pyr)_2CH^+BF_4^-$
ε [$(pyr)_2CH^+BF_4^-$ at 612 nm] = 1.39×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**2b**]$_0$ (mol L^{-1})	A	[$(pyr)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.569	8.185×10^{-6}	
1	3.779×10^{-4}	0.407	5.850×10^{-6}	1.05×10^3
2	7.543×10^{-4}	0.322	4.626×10^{-6}	1.02×10^3
3	1.129×10^{-3}	0.268	3.850×10^{-6}	9.89×10^2
4	1.503×10^{-3}	0.230	3.310×10^{-6}	9.70×10^2
5	1.874×10^{-3}	0.202	2.911×10^{-6}	9.54×10^2
6	2.245×10^{-3}	0.180	2.587×10^{-6}	9.49×10^2
0	0	0.614	8.829×10^{-6}	1.06×10^3
1	3.963×10^{-4}	0.432	6.213×10^{-6}	1.01×10^3
2	7.908×10^{-4}	0.340	4.893×10^{-6}	9.86×10^2
3	1.184×10^{-3}	0.282	4.057×10^{-6}	9.70×10^2
4	1.575×10^{-3}	0.241	3.471×10^{-6}	9.64×10^2
5	1.965×10^{-3}	0.210	3.025×10^{-6}	9.53×10^2
6	2.353×10^{-3}	0.187	2.694×10^{-6}	1.06×10^3
0	0	0.610	8.777×10^{-6}	
1	3.760×10^{-4}	0.430	6.186×10^{-6}	1.11×10^3
2	7.505×10^{-4}	0.342	4.921×10^{-6}	1.04×10^3
3	1.123×10^{-3}	0.284	4.086×10^{-6}	1.01×10^3
4	1.495×10^{-3}	0.244	3.514×10^{-6}	9.92×10^2
5	1.865×10^{-3}	0.214	3.075×10^{-6}	9.82×10^2
6	2.233×10^{-3}	0.191	2.747×10^{-6}	9.68×10^2

K_{av}(20 °C) = 9.99×10^2 L mol^{-1}

Equilibrium constant for the reaction of 1-methylbenzimidazole (**2b**) and $(dma)_2CH^+BF_4^-$
ε [$(dma)_2CH^+BF_4^-$ at 605 nm] = 1.46×10^5 M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**2b**]$_0$ (mol L^{-1})	A	[$(dma)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.624	8.518×10^{-6}	
1	3.604×10^{-5}	0.452	6.175×10^{-6}	1.11×10^4
2	7.177×10^{-5}	0.352	4.814×10^{-6}	1.11×10^4
3	1.072×10^{-4}	0.288	3.934×10^{-6}	1.11×10^4
4	1.423×10^{-4}	0.243	3.319×10^{-6}	1.11×10^4
5	1.945×10^{-4}	0.196	2.684×10^{-6}	1.11×10^4
6	2.460×10^{-4}	0.165	2.252×10^{-6}	1.11×10^4
0	0	0.584	7.973×10^{-6}	
1	3.437×10^{-5}	0.427	5.829×10^{-6}	1.12×10^4
2	6.847×10^{-5}	0.336	4.591×10^{-6}	1.11×10^4
3	1.023×10^{-4}	0.277	3.781×10^{-6}	1.10×10^4
4	1.359×10^{-4}	0.234	3.203×10^{-6}	1.10×10^4
5	2.022×10^{-4}	0.182	2.481×10^{-6}	1.09×10^4
6	2.674×10^{-4}	0.147	2.009×10^{-6}	1.09×10^4
0	0	0.619	8.454×10^{-6}	
1	1.796×10^{-5}	0.517	7.065×10^{-6}	1.17×10^4
2	5.366×10^{-5}	0.393	5.366×10^{-6}	1.12×10^4
3	8.905×10^{-5}	0.315	4.305×10^{-6}	1.11×10^4

4	1.242×10^{-4}	0.262	3.585×10^{-6}	1.11×10^{4}
5	1.590×10^{-4}	0.225	3.070×10^{-6}	1.11×10^{4}
6	1.935×10^{-4}	0.196	2.677×10^{-6}	1.11×10^{4}

K_{av}(20 °C) = 1.11×10^{4} L mol^{-1}

Equilibrium constant for the reaction of 1-methylbenzotriazole (**3b**) and $(mfa)_2CH^+BF_4^-$
ε [$(mfa)_2CH^+BF_4^-$ at 586 nm] = 1.59×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**3b**]$_0$ (mol L^{-1})	A	[$(mfa)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.715	8.985×10^{-6}	
1	2.396×10^{-3}	0.475	5.967×10^{-6}	2.04×10^{2}
2	4.732×10^{-3}	0.355	4.455×10^{-6}	2.05×10^{2}
3	7.011×10^{-3}	0.279	3.500×10^{-6}	2.10×10^{2}
4	9.235×10^{-3}	0.229	2.873×10^{-6}	2.14×10^{2}
5	1.141×10^{-2}	0.194	2.442×10^{-6}	2.16×10^{2}
0	0	0.748	9.402×10^{-6}	
1	2.461×10^{-3}	0.492	6.180×10^{-6}	2.04×10^{2}
2	4.859×10^{-3}	0.364	4.575×10^{-6}	2.07×10^{2}
3	7.197×10^{-3}	0.288	3.616×10^{-6}	2.09×10^{2}
4	9.478×10^{-3}	0.236	2.962×10^{-6}	2.13×10^{2}
5	1.170×10^{-2}	0.199	2.500×10^{-6}	2.16×10^{2}
0	0	0.675	8.483×10^{-6}	
1	2.263×10^{-3}	0.456	5.734×10^{-6}	2.04×10^{2}
2	4.473×10^{-3}	0.341	4.285×10^{-6}	2.09×10^{2}
3	6.633×10^{-3}	0.271	3.402×10^{-6}	2.12×10^{2}
4	8.742×10^{-3}	0.223	2.804×10^{-6}	2.16×10^{2}
5	1.080×10^{-2}	0.189	2.374×10^{-6}	2.20×10^{2}

K_{av}(20 °C) = 2.11×10^{2} L mol^{-1}

Equilibrium constant for the reaction of 1-methylbenzotriazole (**3b**) and $(pfa)_2CH^+BF_4^-$
ε [$(pfa)_2CH^+BF_4^-$ at 592 nm] = 1.27×10^{5} M^{-1} cm^{-1} and d = 0.5 cm

Entry	[**3b**]$_0$ (mol L^{-1})	A	[$(pfa)_2CH^+BF_4^-$]$_{eq}$ (mol L^{-1})	K (L mol^{-1})
0		0.607	9.594×10^{-6}	
1	7.730×10^{-5}	0.370	5.851×10^{-6}	8.60×10^{3}
2	1.540×10^{-4}	0.265	4.187×10^{-6}	8.57×10^{3}
3	2.300×10^{-4}	0.207	3.264×10^{-6}	8.51×10^{3}
4	3.055×10^{-4}	0.171	2.703×10^{-6}	8.34×10^{3}
5	4.546×10^{-4}	0.125	1.970×10^{-6}	8.40×10^{3}
0		0.620	9.788×10^{-6}	
1	7.976×10^{-5}	0.372	5.870×10^{-6}	8.70×10^{3}
2	1.589×10^{-4}	0.264	4.167×10^{-6}	8.67×10^{3}
3	2.373×10^{-4}	0.205	3.231×10^{-6}	8.63×10^{3}
4	3.151×10^{-4}	0.168	2.646×10^{-6}	8.56×10^{3}
5	4.688×10^{-4}	0.123	1.939×10^{-6}	8.51×10^{3}

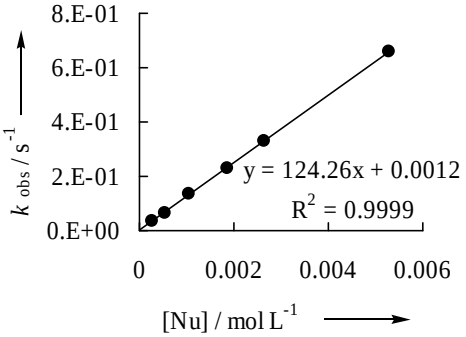
6	6.200×10^{-4}	0.097	1.531×10^{-6}	8.48×10^{3}
0		0.645	1.019×10^{-5}	
1	8.284×10^{-5}	0.381	6.014×10^{-6}	8.74×10^{3}
2	1.650×10^{-4}	0.269	4.254×10^{-6}	8.65×10^{3}
3	2.464×10^{-4}	0.209	3.299×10^{-6}	8.56×10^{3}
4	4.071×10^{-4}	0.143	2.265×10^{-6}	8.52×10^{3}
5	5.652×10^{-4}	0.110	1.735×10^{-6}	8.44×10^{3}
6	7.206×10^{-4}	0.089	1.412×10^{-6}	8.35×10^{3}

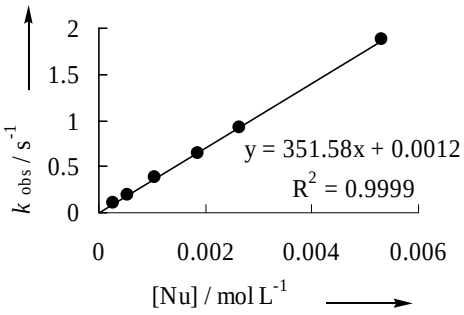
$K_{av}(20\ ^{\circ}C) = 8.54 \times 10^{2}\ L\ mol^{-1}$

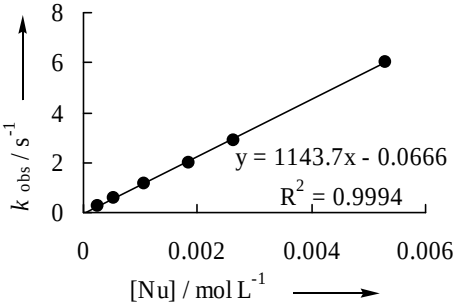
Kinetics for the reactions of amines 1–3 with benzhydrylium ions (Ar_2CH^+) in CH_3CN and DMSO at 20 °C

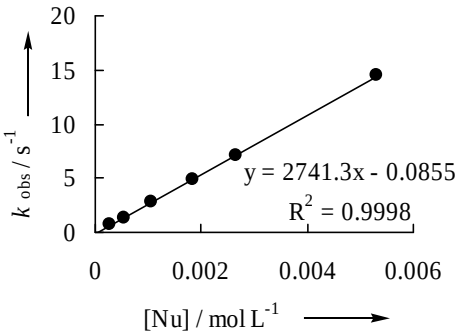
The reactions of imidazoles **1**, benzimidazoles **2**, and benzotriazoles **3** with the colored benzhydrylium tetrafluoroborates were followed photometrically at the vicinity of absorption maxima of Ar_2CH^+ by UV-Vis spectrometry using stopped flow or J&M instrument as described previously.[S1] Al experiments were performed under pseudo-first-order conditions (excess of amines **1**–**3**) at 20 °C in dry CH_3CN or in dry DMSO. First-order rate constants k_{obs} were obtained by least-square fitting of the absorbances to the mono exponential curve $A_t = A_0 \exp(-k_{obs}t) + C$. Because of $k_{obs} = k$[amine], the second-order rate constants k (L mol^{-1} s^{-1}) were derived from the slope of the linear plot of k_{obs} (s^{-1}) vs. [amine].

Kinetics of the reactions of imidazole (**1a**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

$[(ind)_2CH^+]$ (mol L^{-1})	[**1a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
8.50×10^{-6}	2.64×10^{-4}	3.55×10^{-2}		1.24×10^{2}
	5.28×10^{-4}	6.59×10^{-2}		
	1.06×10^{-3}	1.33×10^{-1}		
	1.85×10^{-3}	2.28×10^{-1}		
	2.64×10^{-3}	3.31×10^{-1}		
	5.30×10^{-3}	6.60×10^{-1}		

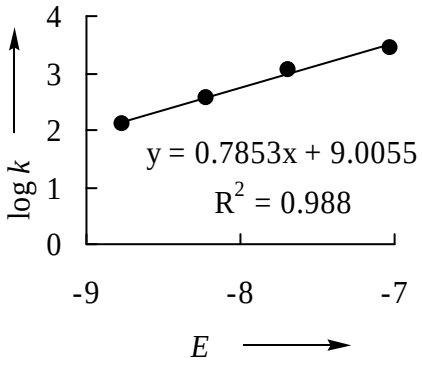
$[(thq)_2CH^+]$ (mol L^{-1})	[**1a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
1.33×10^{-5}	2.64×10^{-4}	1.03×10^{-1}		3.52×10^{2}
	5.28×10^{-4}	1.87×10^{-1}		
	1.06×10^{-3}	3.75×10^{-1}		
	1.85×10^{-3}	6.40×10^{-1}		
	2.64×10^{-3}	9.25×10^{-1}		
	5.30×10^{-3}	1.87		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**1a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
4.08×10^{-6}	2.64×10^{-4}	2.82×10^{-1}		1.14×10^{3}
	5.28×10^{-4}	5.64×10^{-1}		
	1.06×10^{-3}	1.15		
	1.85×10^{-3}	1.98		
	2.64×10^{-3}	2.90		
	5.30×10^{-3}	6.04		

$[(dma)_2CH^+]$ (mol L^{-1})	[**1a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
1.32×10^{-5}	2.64×10^{-4}	7.31×10^{-1}		2.74×10^{3}
	5.28×10^{-4}	1.38		
	1.06×10^{-3}	2.81		
	1.85×10^{-3}	4.87		
	2.64×10^{-3}	7.11		
	5.30×10^{-3}	1.45×10^{1}		

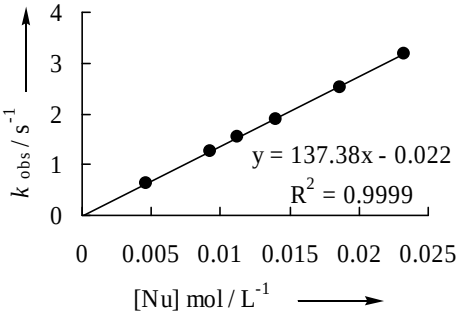
Reactivity parameters for imidazole (1a) in CH_3CN

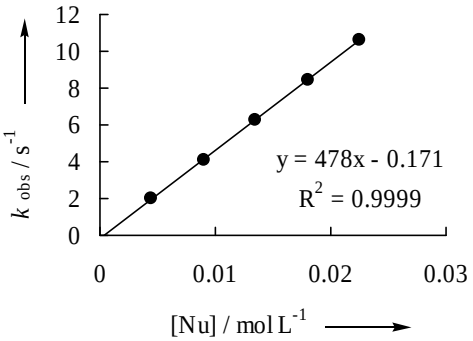
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(ind)_2CH^+$	–8.76	1.24×10^{2}
$(thq)_2CH^+$	–8.22	3.52×10^{2}
$(pyr)_2CH^+$	–7.69	1.14×10^{3}
$(dma)_2CH^+$	–7.02	2.74×10^{3}

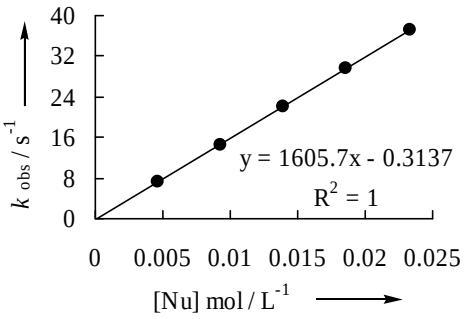


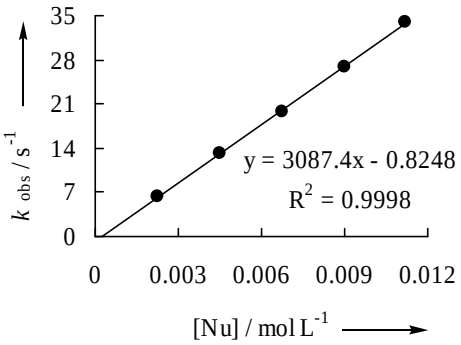
***N* = 11.47**
***s* = 0.79**

Kinetics of the reactions of imidazole (**1a**) with $(Ar)_2CH^+$ in DMSO at 20°C

$[(ind)_2CH^+]$ (mol L^{-1})	[**1a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.58×10^{-5}	4.66×10^{-3}	0.621		1.37×10^2
	9.31×10^{-3}	1.25		
	1.12×10^{-2}	1.53		
	1.40×10^{-2}	1.90		
	1.86×10^{-2}	2.53		
	2.33×10^{-2}	3.18		

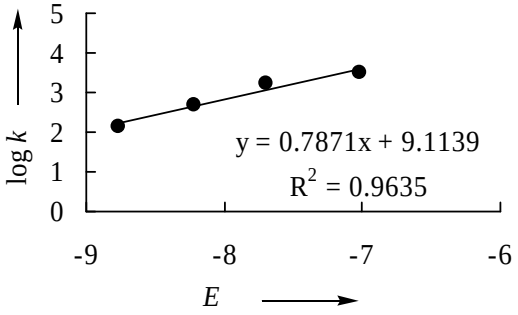
$[(thq)_2CH^+]$ (mol L^{-1})	[**1a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
2.86×10^{-4}	4.50×10^{-3}	2.00		4.78×10^2
	9.00×10^{-3}	4.13		
	1.35×10^{-2}	6.24		
	1.80×10^{-2}	8.44		
	2.25×10^{-2}	10.6		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**1a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.53×10^{-5}	4.66×10^{-3}	7.17		1.61×10^3
	9.31×10^{-3}	14.6		
	1.40×10^{-2}	22.1		
	1.86×10^{-2}	29.5		
	2.33×10^{-2}	37.1		

$[(dma)_2CH^+]$ (mol L^{-1})	[**1a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.76×10^{-5}	2.25×10^{-3}	6.22		3.09×10^3
	4.50×10^{-3}	13.1		
	6.75×10^{-3}	19.8		
	9.00×10^{-3}	26.9		
	1.12×10^{-2}	33.9		

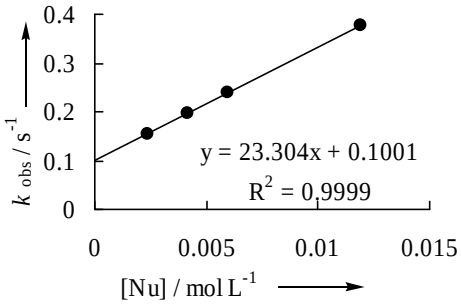
Reactivity parameters for imidazole (**1a**) in DMSO

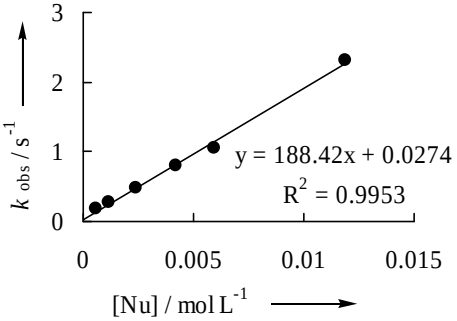
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(ind)_2CH^+$	–8.76	1.37×10^2
$(thq)_2CH^+$	–8.22	4.78×10^2
$(pyr)_2CH^+$	–7.69	1.61×10^3
$(dma)_2CH^+$	–7.02	3.09×10^3

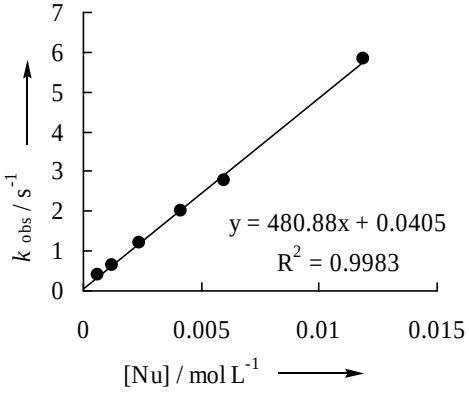


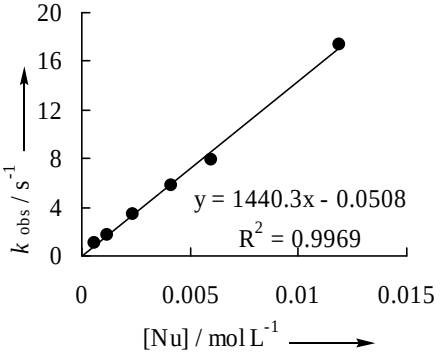
***N* = 11.58**
***s* = 0.79**

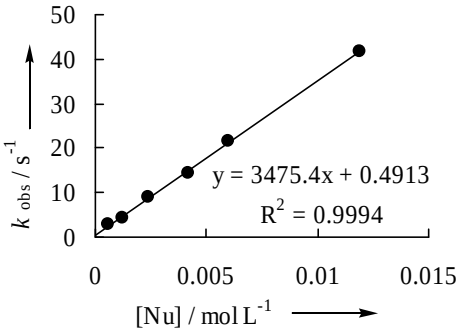
Kinetics of the reactions of 1-methylimidazole (**1b**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

$[(lil)_2CH^+]$ (mol L^{-1})	[**1b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
1.27×10^{-5}	2.38×10^{-3} 4.17×10^{-3} 5.95×10^{-3} 1.19×10^{-2}	1.55×10^{-1} 1.97×10^{-1} 2.40×10^{-1} 3.77×10^{-1}		23.3

$[(ind)_2CH^+]$ (mol L^{-1})	[**1b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
4.94×10^{-6}	5.95×10^{-4} 1.19×10^{-3} 2.38×10^{-3} 4.17×10^{-3} 5.95×10^{-3} 1.19×10^{-2}	1.83×10^{-1} 2.67×10^{-1} 4.83×10^{-1} 7.95×10^{-1} 1.05 2.32		1.88×10^2

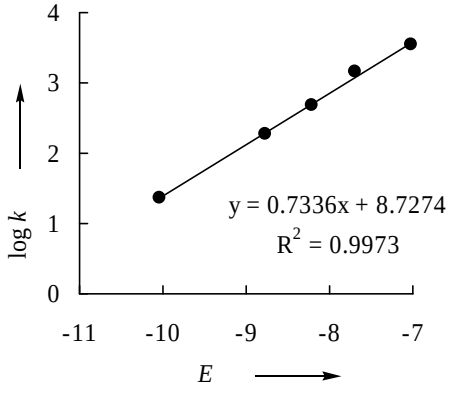
$[(thq)_2CH^+]$ (mol L^{-1})	[**1b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
2.00×10^{-5}	5.95×10^{-4} 1.19×10^{-3} 2.38×10^{-3} 4.17×10^{-3} 5.95×10^{-3} 1.19×10^{-2}	4.09×10^{-1} 6.26×10^{-1} 1.19 2.01 2.76 5.84		4.81×10^2

$[(pyr)_2CH^+]$ (mol L^{-1})	[**1b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
8.15×10^{-6}	5.95×10^{-4}	1.10		1.44×10^3
	1.19×10^{-3}	1.71		
	2.38×10^{-3}	3.46		
	4.17×10^{-3}	5.83		
	5.95×10^{-3}	7.92		
	1.19×10^{-2}	17.4		

$[(dma)_2CH^+]$ (mol L^{-1})	[**1b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
2.06×10^{-5}	5.95×10^{-4}	2.91		3.48×10^3
	1.19×10^{-3}	4.28		
	2.38×10^{-3}	8.86		
	4.17×10^{-3}	1.45×10^1		
	5.95×10^{-3}	2.16×10^1		
	1.19×10^{-2}	4.18×10^1		

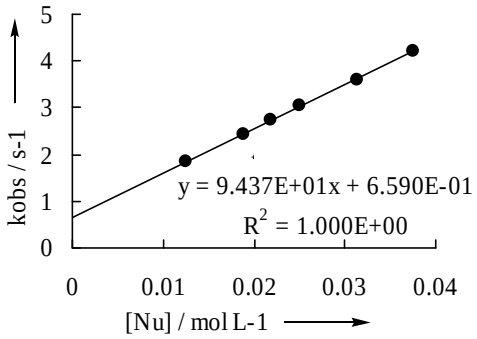
Reactivity parameters for 1-methylimidazole (1b) in CH_3CN

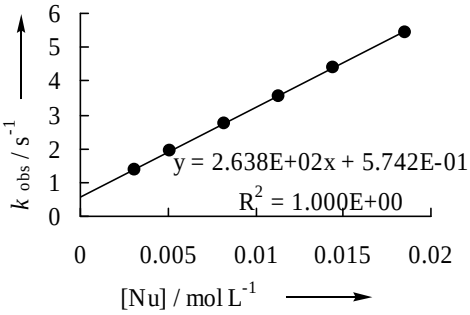
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	2.33×10^1
$(ind)_2CH^+$	–8.76	1.88×10^2
$(thq)_2CH^+$	–8.22	4.81×10^2
$(pyr)_2CH^+$	–7.69	1.44×10^3
$(dma)_2CH^+$	–7.02	3.48×10^3

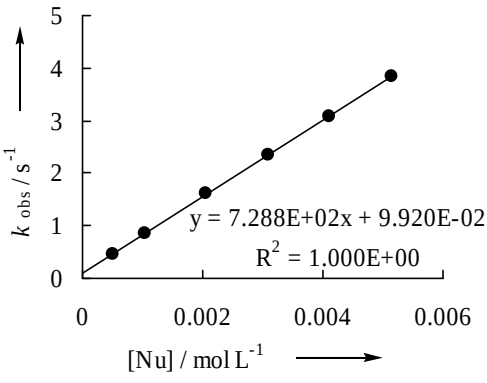


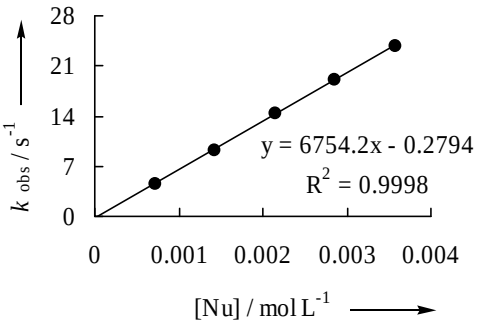
***N* = 11.90**
***s* = 0.73**

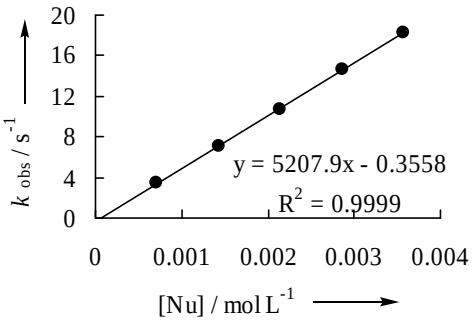
Kinetics of the reactions of 1-phenylimidazole (**1c**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

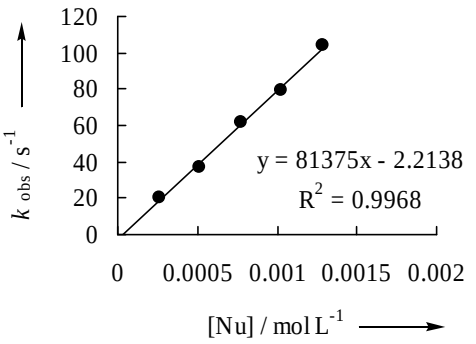
$[(thq)_2CH^+]$ (mol L^{-1})	[**1c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
2.75×10^{-4}	1.25×10^{-2}	1.84		94.4
	1.88×10^{-2}	2.43		
	2.19×10^{-2}	2.73		
	2.51×10^{-2}	3.04		
	3.13×10^{-2}	3.61		
	3.76×10^{-2}	4.21		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**1c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 608 nm	k (M^{-1} s^{-1})
1.68×10^{-5}	3.09×10^{-3}	1.38		2.64×10^2
	5.14×10^{-3}	1.93		
	8.23×10^{-3}	2.76		
	1.13×10^{-2}	3.56		
	1.44×10^{-2}	4.38		
	1.85×10^{-2}	5.45		

$[(dma)_2CH^+]$ (mol L^{-1})	[**1c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 608 nm	k (M^{-1} s^{-1})
1.76×10^{-5}	5.14×10^{-4}	0.465		7.29×10^2
	1.03×10^{-3}	0.848		
	2.06×10^{-3}	1.61		
	3.09×10^{-3}	2.36		
	4.11×10^{-3}	3.09		
	5.14×10^{-3}	3.84		

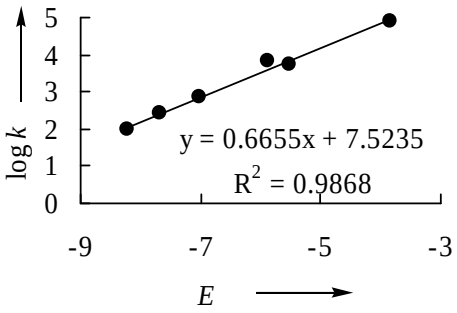
$[(mpa)_2CH^+]$ (mol L^{-1})	[**1c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 613 nm	k (M^{-1} s^{-1})
1.98×10^{-5}	7.15×10^{-4}	4.53		6.75×10^3
	1.43×10^{-3}	9.28		
	2.15×10^{-3}	14.4		
	2.86×10^{-3}	19.1		
	3.58×10^{-3}	23.8		

$[(mor)_2CH^+]$ (mol L^{-1})	[**1c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 613 nm	k (M^{-1} s^{-1})
2.55×10^{-5}	7.15×10^{-4}	3.42		5.21×10^3
	1.43×10^{-3}	7.03		
	2.15×10^{-3}	10.8		
	2.86×10^{-3}	14.6		
	3.58×10^{-3}	18.3		

$[(mfa)_2CH^+]$ (mol L^{-1})	[**1c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 590 nm	k (M^{-1} s^{-1})
1.11×10^5	2.57×10^{-4}	20.1		8.14×10^4
	5.14×10^{-4}	37.4		
	7.71×10^{-4}	62.0		
	1.03×10^{-3}	79.7		
	1.29×10^{-3}	10.4×10^1		

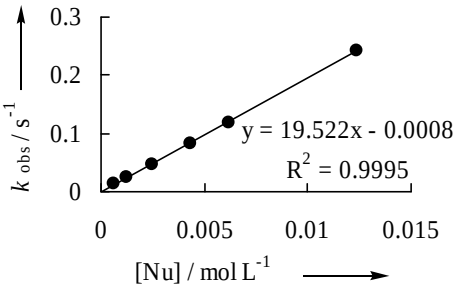
Reactivity parameters for 1-phenylimidazole (1c) in CH_3CN

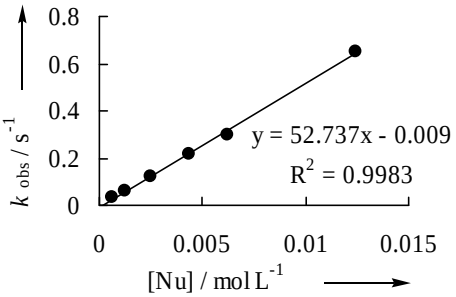
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(thq)_2CH^+$	–8.22	9.44×10^1
$(pyr)_2CH^+$	–7.69	2.64×10^2
$(dma)_2CH^+$	–7.02	7.29×10^2
$(mpa)_2CH^+$	–5.89	6.75×10^3
$(mor)_2CH^+$	–5.53	5.21×10^3
$(mfa)_2CH^+$	–3.85	8.14×10^3

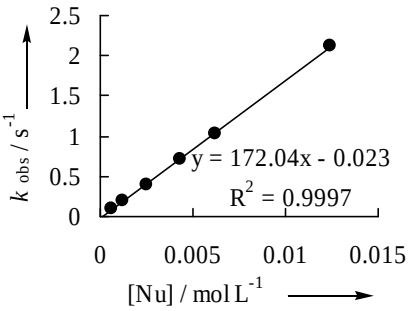


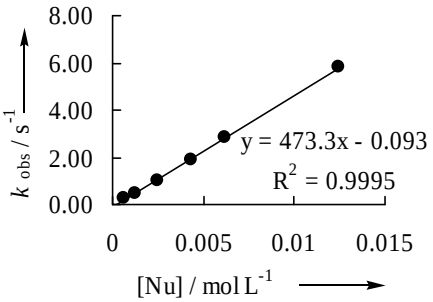
***N* = 11.31**
***s* = 0.67**

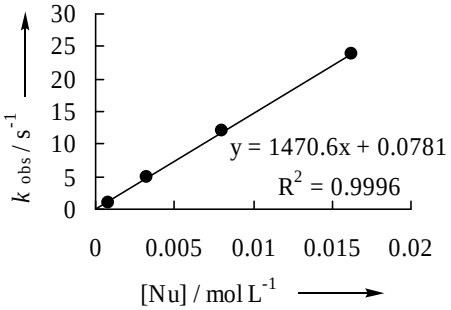
Kinetics of the reactions of 2-methylimidazole (**1d**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

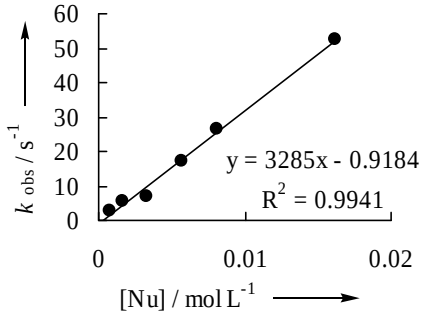
$[(lil)_2CH^+]$ (mol L^{-1})	[**1d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 633 nm	k (M^{-1} s^{-1})
2.29×10^{-6}	6.18×10^{-4}	1.32×10^{-2}		19.5
	1.24×10^{-3}	2.39×10^{-2}		
	2.47×10^{-3}	4.74×10^{-2}		
	4.33×10^{-3}	8.27×10^{-2}		
	6.18×10^{-3}	1.17×10^{-1}		
	1.24×10^{-2}	2.43×10^{-1}		

$[(jul)_2CH^+]$ (mol L^{-1})	[**1d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 636 nm	k (M^{-1} s^{-1})
5.75×10^{-6}	6.18×10^{-4}	3.30×10^{-2}		52.7
	1.24×10^{-3}	5.94×10^{-2}		
	2.47×10^{-3}	1.21×10^{-1}		
	4.33×10^{-3}	2.14×10^{-1}		
	6.18×10^{-3}	3.01×10^{-1}		
	1.24×10^{-2}	6.54×10^{-1}		

$[(ind)_2CH^+]$ (mol L^{-1})	[**1d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 619 nm	k (M^{-1} s^{-1})
7.74×10^{-6}	6.18×10^{-4}	1.04×10^{-1}		1.72×10^{2}
	1.24×10^{-3}	1.93×10^{-1}		
	2.47×10^{-3}	3.88×10^{-1}		
	4.33×10^{-3}	7.13×10^{-1}		
	6.18×10^{-3}	1.03		
	1.24×10^{-2}	2.12		

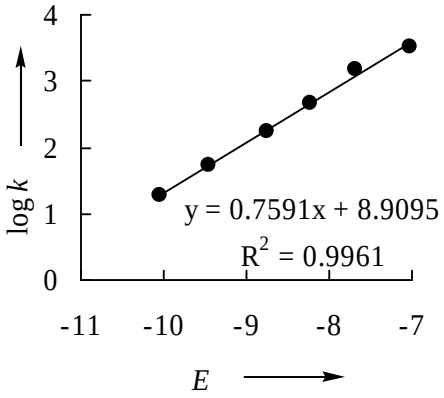
$[(thq)_2CH^+]$ (mol L^{-1})	[**1d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 622 nm	k (M^{-1} s^{-1})
1.93×10^{-5}	6.18×10^{-4}	2.73×10^{-1}		4.73×10^{2}
	1.24×10^{-3}	5.01×10^{-1}		
	2.47×10^{-3}	1.01		
	4.33×10^{-3}	1.93		
	6.18×10^{-3}	2.82		
	1.24×10^{-2}	5.80		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**1d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 608 nm	k (M^{-1} s^{-1})
3.71×10^{-6}	8.07×10^{-4}	1.03		1.47×10^{3}
	3.23×10^{-3}	5.01		
	8.07×10^{-3}	12.1		
	1.62×10^{-2}	23.8		

$[(dma)_2CH^+]$ (mol L^{-1})	[**1d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 608 nm	k (M^{-1} s^{-1})
1.87×10^{-5}	8.07×10^{-4}	2.88		3.29×10^{3}
	1.62×10^{-3}	5.41		
	3.23×10^{-3}	7.07		
	5.65×10^{-3}	17.1		
	8.07×10^{-3}	26.5		
	1.62×10^{-2}	52.4		

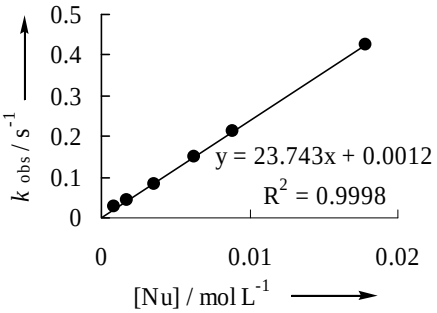
Reactivity parameters for 2-methylimidazole (1d) in CH_3CN

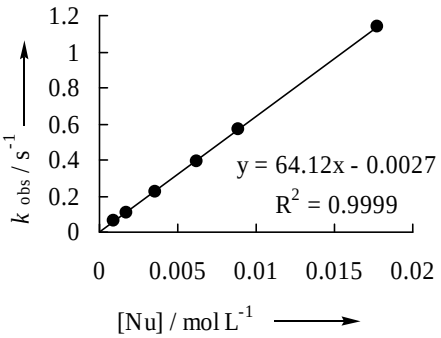
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	1.95×10^1
$(jul)_2CH^+$	–9.45	5.27×10^1
$(ind)_2CH^+$	–8.76	1.72×10^2
$(thq)_2CH^+$	–8.22	4.73×10^2
$(pyr)_2CH^+$	–7.69	1.47×10^3
$(dma)_2CH^+$	–7.02	3.29×10^3

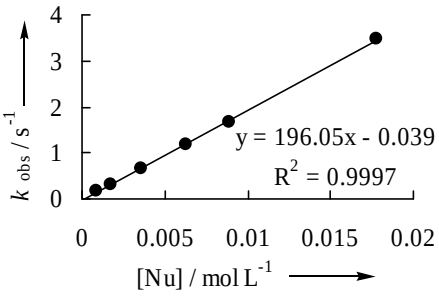


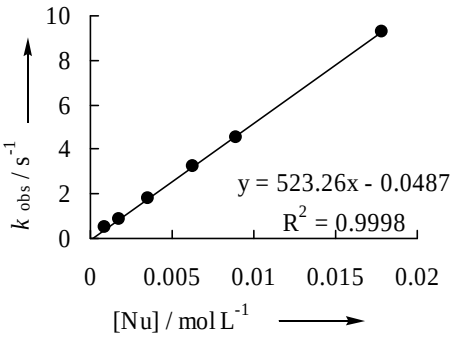
***N* = 11.74**
***s* = 0.76**

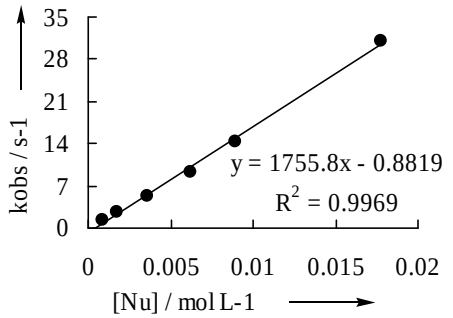
Kinetics of the reactions of 4-methylimidazole (**1e**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

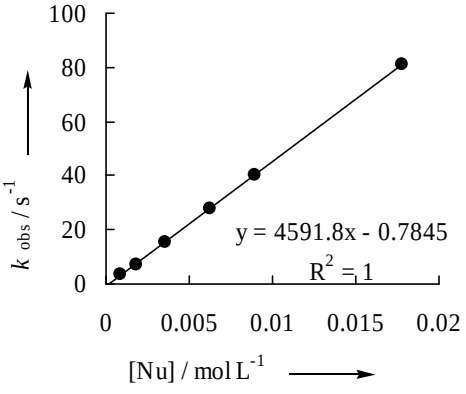
$[(lil)_2CH^+]$ (mol L^{-1})	[**1e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
1.27×10^{-5}	8.90×10^{-4}	2.58×10^{-2}		23.7
	1.78×10^{-3}	4.21×10^{-2}		
	3.56×10^{-3}	8.33×10^{-2}		
	6.25×10^{-3}	1.48×10^{-1}		
	8.90×10^{-3}	2.14×10^{-1}		
	1.78×10^{-2}	4.24×10^{-1}		

$[(jul)_2CH^+]$ (mol L^{-1})	[**1e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
1.19×10^{-5}	8.90×10^{-4}	6.18×10^{-2}		64.1
	1.78×10^{-3}	1.10×10^{-1}		
	3.56×10^{-3}	2.20×10^{-1}		
	6.25×10^{-3}	3.95×10^{-1}		
	8.90×10^{-3}	5.69×10^{-1}		
	1.78×10^{-2}	1.14		

$[(ind)_2CH^+]$ (mol L^{-1})	[**1e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
6.20×10^{-6}	8.90×10^{-4}	1.66×10^{-1}		1.96×10^2
	1.78×10^{-3}	3.17×10^{-1}		
	3.56×10^{-3}	6.44×10^{-1}		
	6.25×10^{-3}	1.17		
	8.90×10^{-3}	1.68		
	1.78×10^{-2}	3.47		

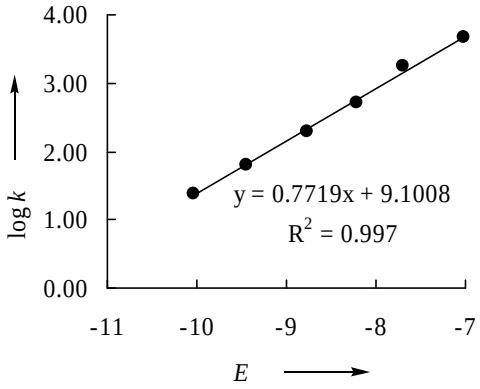
$[(thq)_2CH^+]$ (mol L^{-1})	[**1e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
2.00×10^{-5}	8.90×10^{-4}	4.69×10^{-1}		5.23×10^{2}
	1.78×10^{-3}	8.90×10^{-1}		
	3.56×10^{-3}	1.78		
	6.25×10^{-3}	3.23		
	8.90×10^{-3}	4.54		
	1.78×10^{-2}	9.30		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**1e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
8.15×10^{-5}	8.90×10^{-4}	1.34		1.76×10^{3}
	1.78×10^{-3}	2.52		
	3.56×10^{-3}	5.33		
	6.25×10^{-3}	9.21		
	8.90×10^{-3}	14.2		
	1.78×10^{-2}	30.9		

$[(dma)_2CH^+]$ (mol L^{-1})	[**1e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
1.03×10^{-5}	8.90×10^{-4}	3.65		4.59×10^{3}
	1.78×10^{-3}	7.15		
	3.56×10^{-3}	1.55×10^{1}		
	6.25×10^{-3}	2.78×10^{1}		
	8.90×10^{-3}	4.01×10^{1}		
	1.78×10^{-2}	8.10×10^{1}		

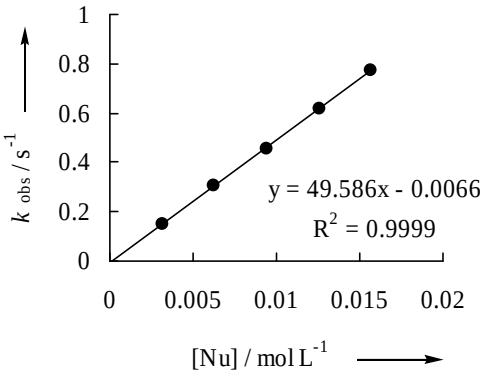
Reactivity parameters for 4-methylimidazole (1e) in CH_3CN

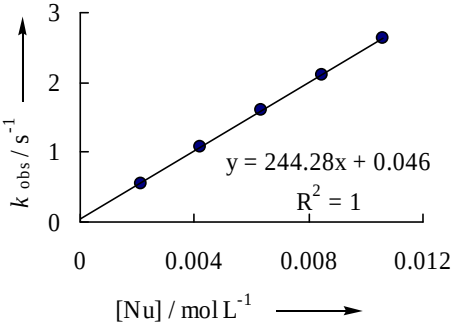
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	2.37×10^1
$(jul)_2CH^+$	–9.45	6.41×10^1
$(ind)_2CH^+$	–8.76	1.96×10^2
$(thq)_2CH^+$	–8.22	5.23×10^2
$(pyr)_2CH^+$	–7.69	1.76×10^3
$(dma)_2CH^+$	–7.02	4.59×10^3

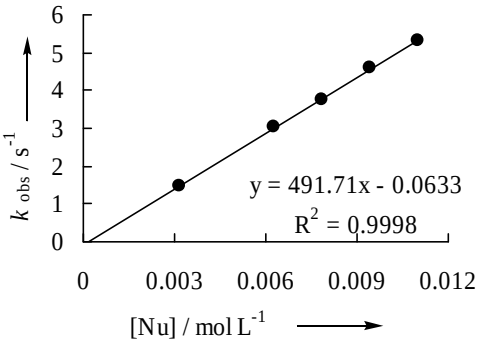


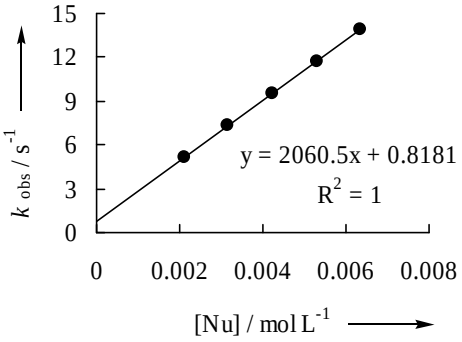
***N* = 11.79**
***s* = 0.77**

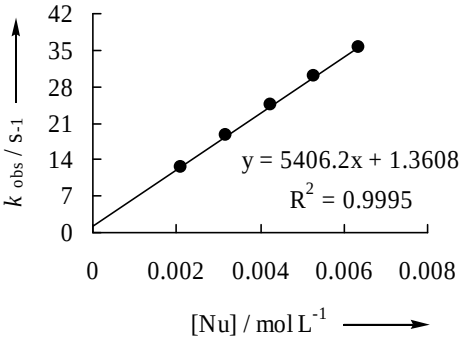
Kinetics of the reactions of 2,4-dimethylimidazole (**1f**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

$[(jul)_2CH^+]$ (mol L^{-1})	[**1f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 635 nm	k (M^{-1} s^{-1})
1.71×10^{-5}	3.14×10^{-3}	0.150		49.6
	6.28×10^{-3}	0.306		
	9.42×10^{-3}	0.457		
	1.26×10^{-2}	0.618		
	1.57×10^{-2}	0.774		

$[(ind)_2CH^+]$ (mol L^{-1})	[**1f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 612 nm	k (M^{-1} s^{-1})
1.68×10^{-5}	2.12×10^{-3}	0.559		2.44×10^2
	4.23×10^{-3}	1.09		
	6.35×10^{-3}	1.59		
	8.46×10^{-3}	2.12		
	1.06×10^{-2}	2.63		

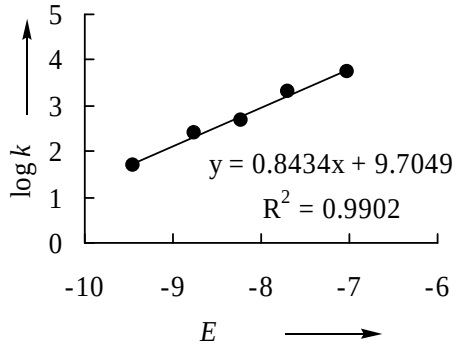
$[(thq)_2CH^+]$ (mol L^{-1})	[**1f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
2.50×10^{-4}	3.14×10^{-3}	1.49		4.92×10^2
	6.28×10^{-3}	3.03		
	7.85×10^{-3}	3.76		
	9.42×10^{-3}	4.59		
	1.10×10^{-2}	5.34		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**1f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 612 nm	k (M^{-1} s^{-1})
1.68×10^{-5}	2.12×10^{-3}	5.16		2.06×10^3
	3.17×10^{-3}	7.38		
	4.23×10^{-3}	9.55		
	5.29×10^{-3}	11.7		
	6.35×10^{-3}	13.9		

$[(dma)_2CH^+]$ (mol L^{-1})	[**1f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 605 nm	k (M^{-1} s^{-1})
1.75×10^{-5}	2.12×10^{-3}	12.6		5.41×10^3
	3.17×10^{-3}	18.6		
	4.23×10^{-3}	24.5		
	5.29×10^{-3}	30.0		
	6.35×10^{-3}	35.5		

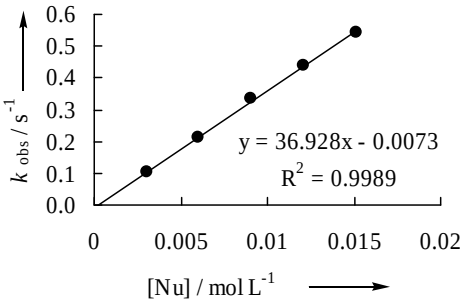
Reactivity parameters for 2,4-dimethylimidazole (1f) in CH_3CN

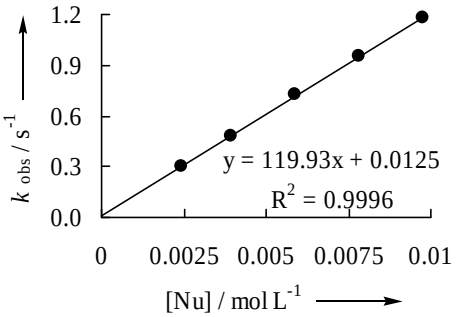
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(jul)_2CH^+$	–9.45	4.96×10^1
$(ind)_2CH^+$	–8.76	2.44×10^2
$(thq)_2CH^+$	–8.22	4.92×10^2
$(pyr)_2CH^+$	–7.69	2.06×10^3
$(dma)_2CH^+$	–7.02	5.41×10^3

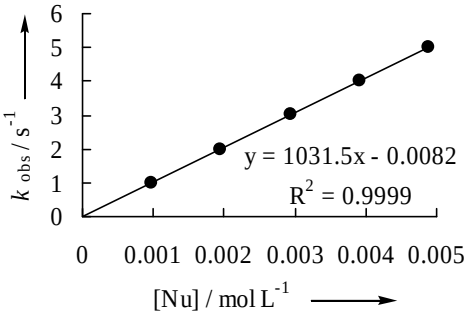


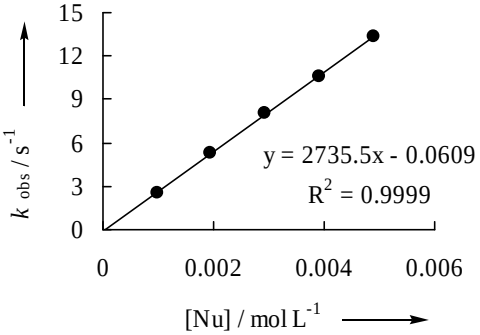
***N* = 11.51**
***s* = 0.84**

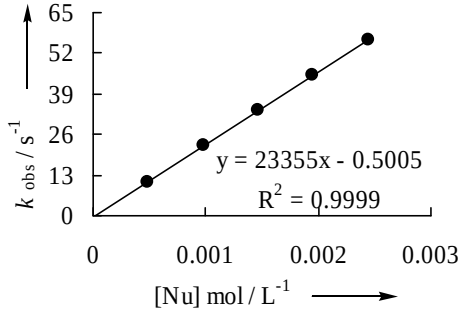
Kinetics of the Reactions of 1-trimethylsilylimidazole (**1g**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

$[(jul)_2CH^+]$ (mol L^{-1})	[**1g**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 635 nm	k (M^{-1} s^{-1})
1.71×10^{-5}	3.02×10^{-3}	0.102		36.9
	6.04×10^{-3}	0.212		
	9.05×10^{-3}	0.337		
	1.21×10^{-2}	0.439		
	1.51×10^{-2}	0.546		

$[(ind)_2CH^+]$ (mol L^{-1})	[**1g**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
1.48×10^{-5}	2.44×10^{-3}	0.299		1.20×10^2
	3.91×10^{-3}	0.482		
	5.86×10^{-3}	0.724		
	7.82×10^{-3}	0.953		
	9.77×10^{-3}	1.18		

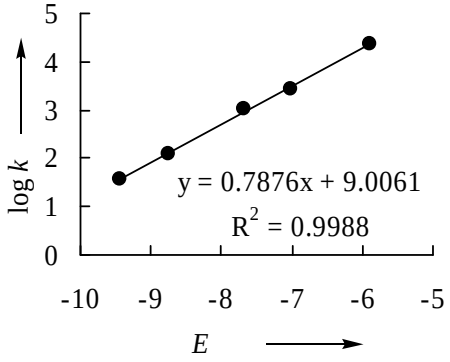
$[(pyr)_2CH^+]$ (mol L^{-1})	[**1g**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
1.68×10^{-5}	9.77×10^{-4}	0.990		1.03×10^3
	1.95×10^{-3}	2.00		
	2.93×10^{-3}	3.04		
	3.91×10^{-3}	4.03		
	4.89×10^{-3}	5.01		

$[(dma)_2CH^+]$ (mol L^{-1})	[**1g**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
1.76×10^{-5}	9.77×10^{-4}	2.57		2.74×10^3
	1.95×10^{-3}	5.29		
	2.93×10^{-3}	8.03		
	3.91×10^{-3}	10.6		
	4.89×10^{-3}	13.3		

$[(mpa)_2CH^+]$ (mol L^{-1})	[**1g**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
1.58×10^{-5}	4.89×10^{-4}	10.8		2.34×10^4
	9.77×10^{-4}	22.3		
	1.47×10^{-3}	33.9		
	1.95×10^{-3}	45.1		
	2.44×10^{-3}	56.4		

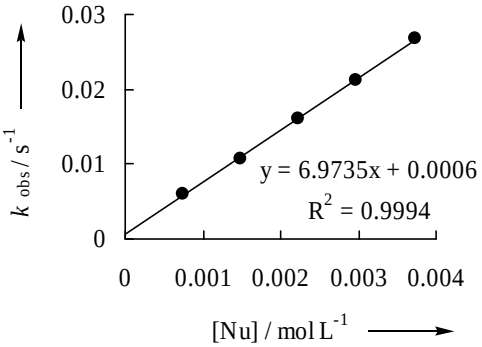
Reactivity parameters for 1-trimethylsilylimidazole (1g) in CH_3CN

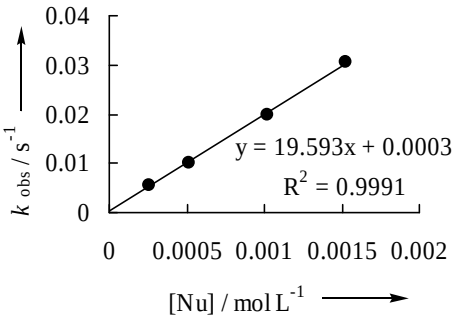
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(jul)_2CH^+$	–9.45	3.69×10^1
$(ind)_2CH^+$	–8.76	1.20×10^2
$(pyr)_2CH^+$	–7.69	1.02×10^2
$(dma)_2CH^+$	–7.02	2.74×10^3
$(mpa)_2CH^+$	–5.89	2.34×10^4

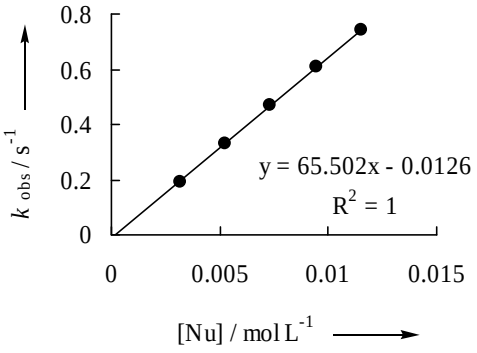


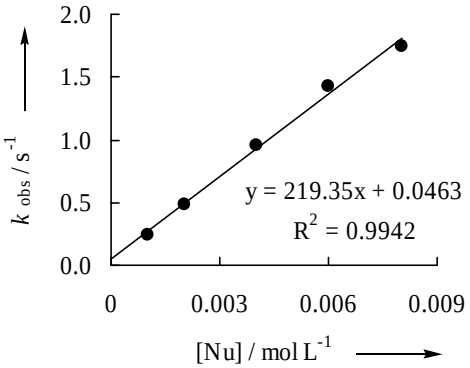
***N* = 11.43**
***s* = 0.79**

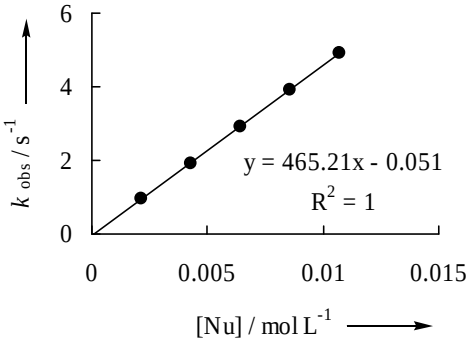
Kinetics of the reactions of benzimidazole (**2a**) with $(Ar)_2CH^+$ in DMSO at 20°C

$[(jul)_2CH^+]$ (mol L^{-1})	[**2a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 635 nm	k (M^{-1} s^{-1})
1.84×10^{-5}	7.47×10^{-4}	6.04×10^{-3}		6.97
1.83×10^{-5}	1.49×10^{-3}	1.08×10^{-2}		
1.83×10^{-5}	2.23×10^{-3}	1.60×10^{-2}		
1.83×10^{-5}	2.97×10^{-3}	2.12×10^{-2}		
1.84×10^{-5}	3.73×10^{-3}	2.68×10^{-2}		

$[(ind)_2CH^+]$ (mol L^{-1})	[**2a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.96×10^{-5}	2.57×10^{-4}	5.66×10^{-3}		19.6
1.95×10^{-5}	5.11×10^{-4}	1.01×10^{-2}		
1.95×10^{-5}	1.02×10^{-3}	1.99×10^{-2}		
1.94×10^{-5}	1.53×10^{-3}	3.05×10^{-2}		

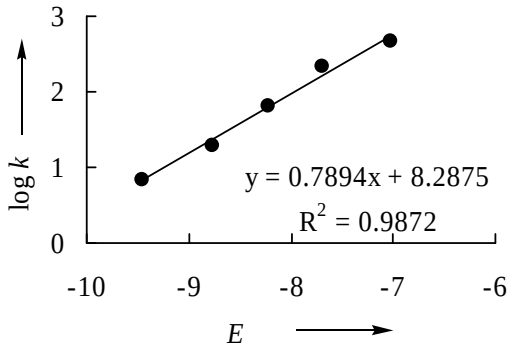
$[(thq)_2CH^+]$ (mol L^{-1})	[**2a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
4.74×10^{-4}	3.15×10^{-3}	0.194		65.5
	5.25×10^{-3}	0.331		
	7.35×10^{-3}	0.469		
	9.45×10^{-3}	0.606		
	1.15×10^{-2}	0.741		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**2a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
2.14×10^{-5}	1.00×10^{-3}	0.237		2.19×10^2
	2.01×10^{-3}	0.478		
	4.01×10^{-3}	0.9958		
	6.02×10^{-3}	1.44		
	8.03×10^{-3}	1.75		

$[(dma)_2CH^+]$ (mol L^{-1})	[**2a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 613 nm	k (M^{-1} s^{-1})
1.50×10^{-5}	2.13×10^{-3}	0.950		4.65×10^2
	4.27×10^{-3}	1.93		
	6.40×10^{-3}	2.91		
	8.54×10^{-3}	3.93		
	1.07×10^{-2}	4.93		

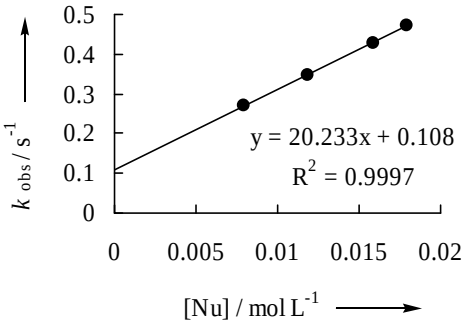
Reactivity parameters for benzimidazole (2a) in DMSO

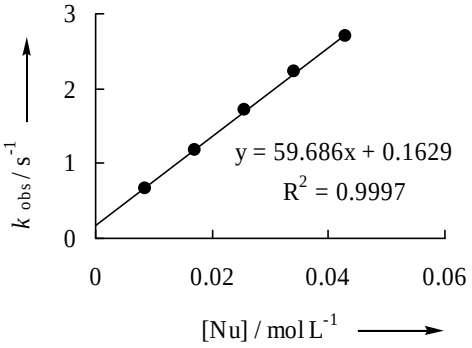
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(jul)_2CH^+$	–9.45	6.97
$(ind)_2CH^+$	–8.76	1.96×10^1
$(thq)_2CH^+$	–8.22	6.55×10^1
$(pyr)_2CH^+$	–7.69	2.19×10^2
$(dma)_2CH^+$	–7.02	4.65×10^2

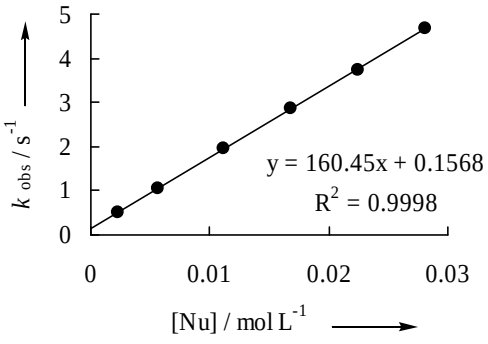


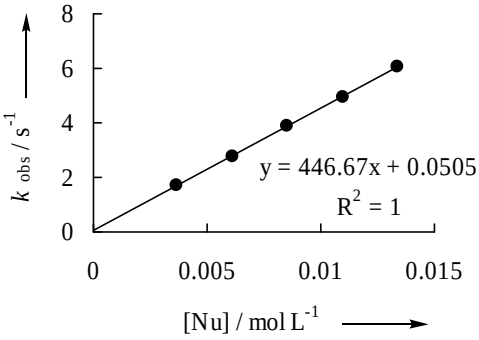
N = 10.50
s = 0.79

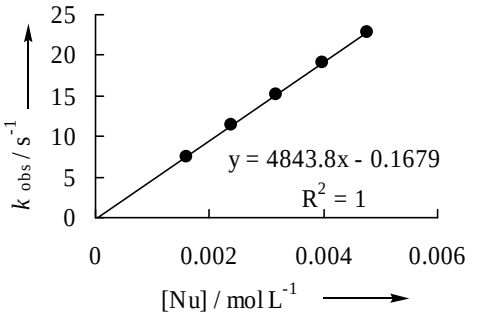
Kinetics of the reactions of 1-methylbenzimidazole (**2b**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

$[(ind)_2CH^+]$ (mol L^{-1})	[**2b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
2.85×10^{-5}	7.94×10^{-3}	0.270		20.2
	1.19×10^{-2}	0.347		
	1.59×10^{-2}	0.429		
	1.79×10^{-2}	0.471		

$[(thq)_2CH^+]$ (mol L^{-1})	[**2b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
2.65×10^{-5}	8.56×10^{-3}	0.666		59.7
	1.71×10^{-2}	1.18		
	2.57×10^{-2}	1.71		
	3.42×10^{-2}	2.22		
	4.28×10^{-2}	2.70		

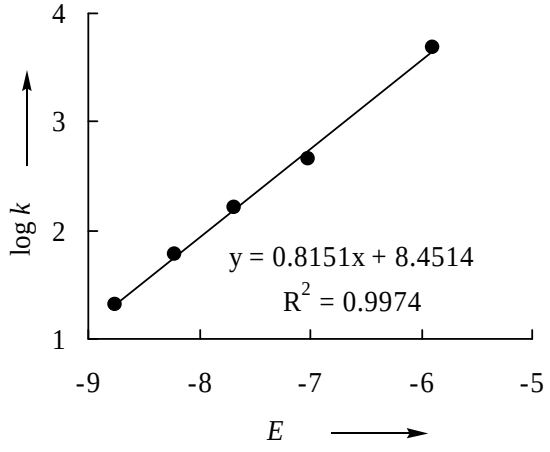
$[(pyr)_2CH^+]$ (mol L^{-1})	[**2b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 611 nm	k (M^{-1} s^{-1})
2.84×10^{-5}	2.25×10^{-3}	0.515		1.60×10^2
	5.62×10^{-3}	1.05		
	1.12×10^{-2}	1.97		
	1.68×10^{-2}	2.87		
	2.25×10^{-2}	3.73		
	2.81×10^{-2}	4.68		

$[(dma)_2CH^+]$ (mol L^{-1})	[**2b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
3.27×10^{-5}	3.66×10^{-3}	1.68		4.47×10^2
	6.10×10^{-3}	2.78		
	8.55×10^{-3}	3.88		
	1.10×10^{-2}	4.95		
	1.34×10^{-2}	6.04		

$[(mpa)_2CH^+]$ (mol L^{-1})	[**2b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
3.27×10^{-5}	1.59×10^{-3}	7.51		4.84×10^3
	2.38×10^{-3}	11.4		
	3.17×10^{-3}	15.2		
	3.97×10^{-3}	19.0		
	4.76×10^{-3}	22.9		

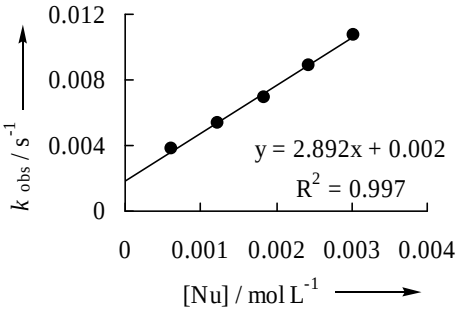
Reactivity parameters for N-methylbenzimidazole (2b) in CH_3CN

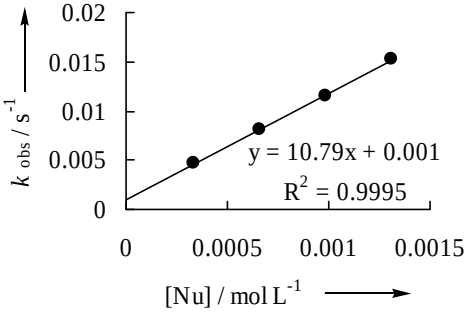
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(ind)_2CH^+$	–8.76	2.02×10^1
$(thq)_2CH^+$	–8.22	5.99×10^1
$(pyr)_2CH^+$	–7.69	1.60×10^2
$(dma)_2CH^+$	–7.02	4.47×10^2
$(mpa)_2CH^+$	–5.89	4.84×10^3

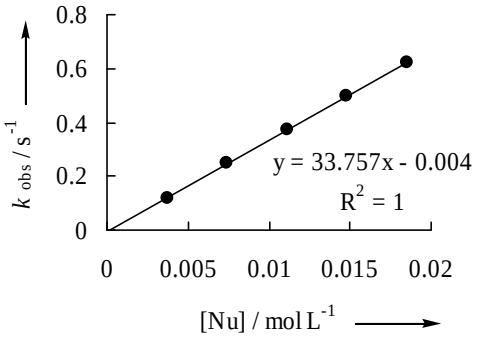


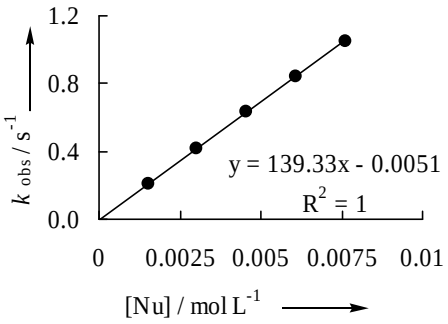
***N* = 10.37**
***s* = 0.82**

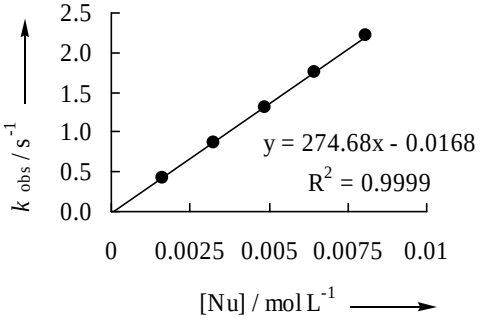
Kinetics of the reactions of 2-methylbenzimidazole (**2c**) with $(Ar)_2CH^+$ in DMSO at 20°C

$[(jul)_2CH^+]$ (mol L^{-1})	[**2c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 635 nm	k (M^{-1} s^{-1})
1.85×10^{-5}	6.23×10^{-4}	3.80×10^{-3}		2.89
1.82×10^{-5}	1.23×10^{-3}	5.33×10^{-3}		
1.82×10^{-5}	1.84×10^{-3}	6.94×10^{-3}		
1.80×10^{-5}	2.43×10^{-3}	8.86×10^{-3}		
1.80×10^{-5}	3.04×10^{-3}	1.08×10^{-2}		

$[(ind)_2CH^+]$ (mol L^{-1})	[**2c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.94×10^{-5}	3.30×10^{-4}	4.66×10^{-3}		10.8
1.94×10^{-5}	6.61×10^{-4}	8.07×10^{-3}		
1.93×10^{-5}	9.86×10^{-4}	1.16×10^{-2}		
1.93×10^{-5}	1.31×10^{-3}	1.53×10^{-2}		

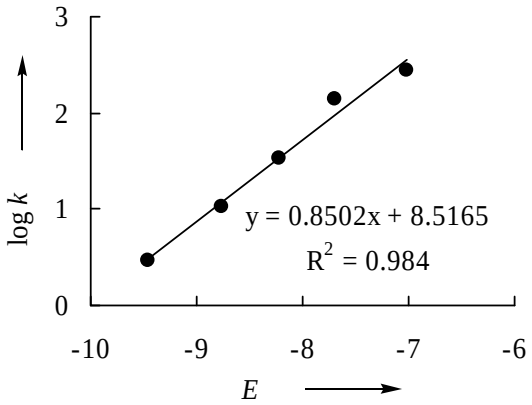
$[(thq)_2CH^+]$ (mol L^{-1})	[**2c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 618 nm	k (M^{-1} s^{-1})
4.74×10^{-4}	3.71×10^{-3}	0.121		33.8
	7.41×10^{-3}	0.246		
	1.11×10^{-2}	0.371		
	1.48×10^{-2}	0.496		
	1.85×10^{-2}	0.620		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**2c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
3.00×10^{-5}	1.52×10^{-3}	0.209		1.39×10^2
	3.04×10^{-3}	0.416		
	4.56×10^{-3}	0.629		
	6.08×10^{-3}	0.844		
	7.60×10^{-3}	1.05		

$[(dma)_2CH^+]$ (mol L^{-1})	[**2c**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 613 nm	k (M^{-1} s^{-1})
2.82×10^{-5}	1.62×10^{-3}	0.430		2.75×10^2
	3.23×10^{-3}	0.874		
	4.85×10^{-3}	1.31		
	6.46×10^{-3}	1.75		
	8.08×10^{-3}	2.21		

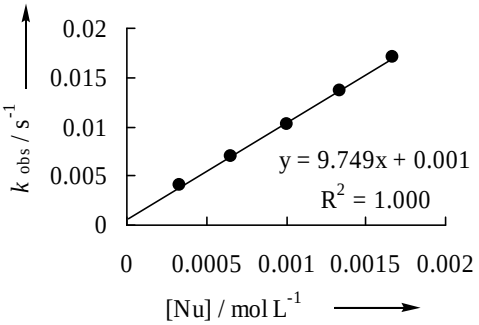
Reactivity parameters for 2-methylbenzimidazole (2c) in DMSO

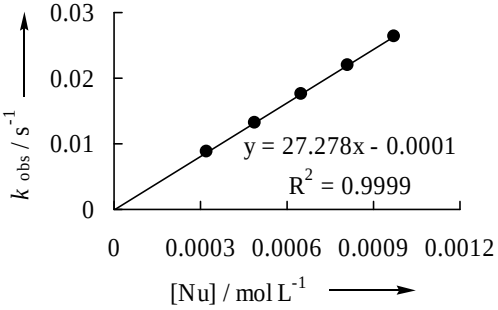
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(jul)_2CH^+$	–9.45	2.89
$(ind)_2CH^+$	–8.76	1.08×10^1
$(thq)_2CH^+$	–8.22	3.38×10^1
$(pyr)_2CH^+$	–7.69	1.39×10^2
$(dma)_2CH^+$	–7.02	2.75×10^2

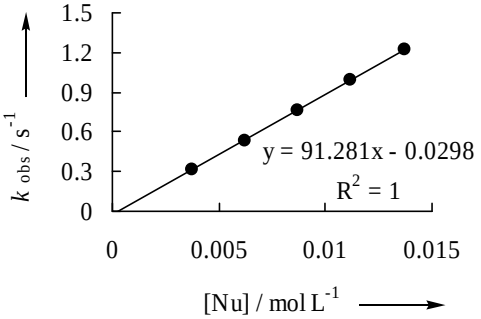


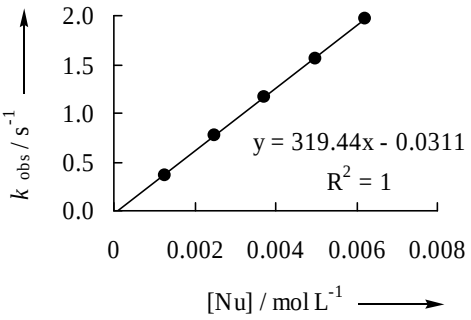
***N* = 10.02**
***s* = 0.85**

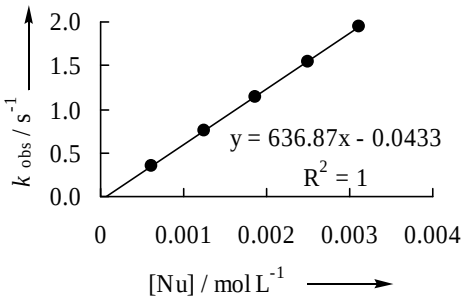
Kinetics of the reactions of 5-methylbenzimidazole (**2d**) with $(Ar)_2CH^+$ in DMSO at 20°C

$[(jul)_2CH^+]$ (mol L^{-1})	[**2d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 645 nm	k (M^{-1} s^{-1})
1.51×10^{-5}	3.35×10^{-4}	4.02×10^{-3}		9.75
1.46×10^{-5}	6.48×10^{-4}	6.92×10^{-3}		
1.51×10^{-5}	1.01×10^{-3}	1.03×10^{-2}		
1.50×10^{-5}	1.34×10^{-3}	1.37×10^{-2}		
1.50×10^{-5}	1.67×10^{-3}	1.70×10^{-2}		

$[(ind)_2CH^+]$ (mol L^{-1})	[**2d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.12×10^{-5}	3.25×10^{-4}	8.78×10^{-3}		27.3
1.12×10^{-5}	4.89×10^{-4}	1.32×10^{-2}		
1.11×10^{-5}	6.49×10^{-4}	1.75×10^{-2}		
1.12×10^{-5}	8.13×10^{-4}	2.20×10^{-2}		
1.11×10^{-5}	9.71×10^{-4}	2.64×10^{-2}		

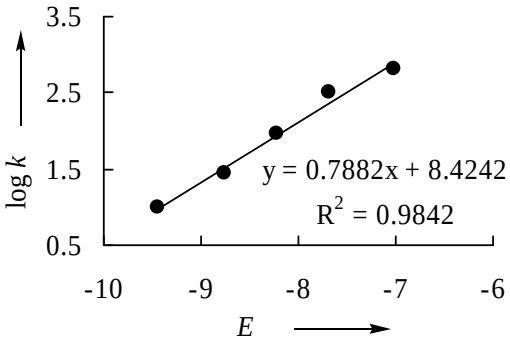
$[(thq)_2CH^+]$ (mol L^{-1})	[**2d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 618 nm	k (M^{-1} s^{-1})
3.06×10^{-5}	3.74×10^{-3}	0.313		91.3
	6.23×10^{-3}	0.537		
	8.72×10^{-3}	0.765		
	1.12×10^{-2}	0.995		
	1.37×10^{-2}	1.22		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**2d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
3.33×10^{-5}	1.25×10^{-3}	0.368		3.19×10^2
	2.49×10^{-3}	0.767		
	3.74×10^{-3}	1.16		
	4.98×10^{-3}	1.56		
	6.23×10^{-3}	1.96		

$[(dma)_2CH^+]$ (mol L^{-1})	[**2d**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 613 nm	k (M^{-1} s^{-1})
3.53×10^{-5}	6.23×10^{-4}	0.36		6.37×10^2
	1.25×10^{-3}	0.75		
	1.87×10^{-3}	1.14		
	2.49×10^{-3}	1.55		
	3.12×10^{-3}	1.94		

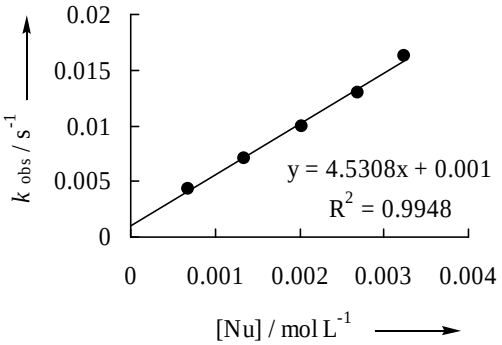
Reactivity parameters for 5-methylbenzimidazole (2d) in DMSO

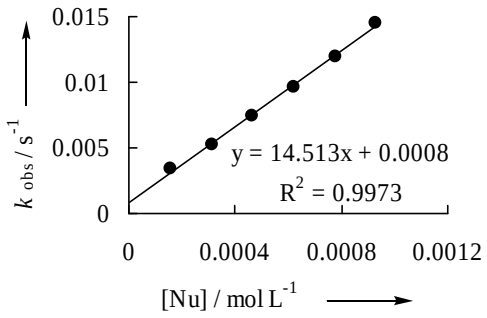
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(jul)_2CH^+$	–9.45	9.75
$(ind)_2CH^+$	–8.76	2.73×10^1
$(thq)_2CH^+$	–8.22	9.13×10^1
$(pyr)_2CH^+$	–7.69	3.19×10^2
$(dma)_2CH^+$	–7.02	6.37×10^2

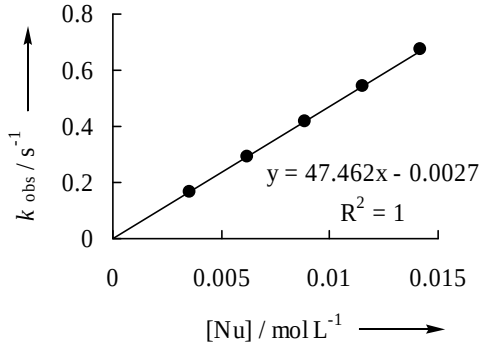


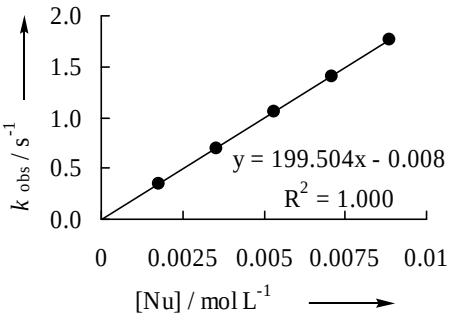
N = 10.69
s = 0.79

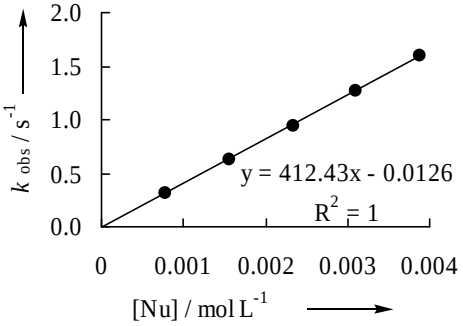
Kinetics of the reactions of 2,5-dimethylbenzimidazole (**2e**) with $(Ar)_2CH^+$ in DMSO at 20°C

$[(jul)_2CH^+]$ (mol L^{-1})	[**2e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 645 nm	k (M^{-1} s^{-1})
1.90×10^{-5}	6.78×10^{-4}	4.38×10^{-3}		4.53
1.89×10^{-5}	1.35×10^{-3}	7.04×10^{-3}		
1.88×10^{-5}	2.02×10^{-3}	1.00×10^{-2}		
1.89×10^{-5}	2.70×10^{-3}	1.29×10^{-2}		
1.82×10^{-5}	3.25×10^{-3}	1.62×10^{-2}		

$[(ind)_2CH^+]$ (mol L^{-1})	[**2e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.72×10^{-5}	1.56×10^{-4}	3.39×10^{-3}		14.5
1.72×10^{-5}	3.12×10^{-4}	5.19×10^{-3}		
1.71×10^{-5}	4.67×10^{-4}	7.44×10^{-3}		
1.70×10^{-5}	6.19×10^{-4}	9.65×10^{-3}		
1.71×10^{-5}	7.75×10^{-4}	1.20×10^{-2}		
1.70×10^{-5}	9.28×10^{-4}	1.45×10^{-2}		

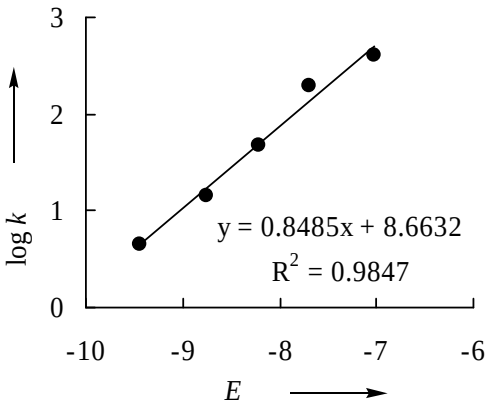
$[(thq)_2CH^+]$ (mol L^{-1})	[**2e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 618 nm	k (M^{-1} s^{-1})
3.62×10^{-5}	3.55×10^{-3}	0.166		47.5
	6.21×10^{-3}	0.292		
	8.88×10^{-3}	0.429		
	1.15×10^{-2}	0.542		
	1.42×10^{-2}	0.672		

$[(pyr)_2CH^+]$ (mol L^{-1})	[**2e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.71×10^{-5}	1.78×10^{-3}	0.348		2.00×10^2
	3.55×10^{-3}	0.699		
	5.33×10^{-3}	1.06		
	7.10×10^{-3}	1.41		
	8.88×10^{-3}	1.77		

$[(dma)_2CH^+]$ (mol L^{-1})	[**2e**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 613 nm	k (M^{-1} s^{-1})
3.13×10^{-5}	7.78×10^{-4}	0.310		4.12×10^2
	1.56×10^{-3}	0.629		
	2.33×10^{-3}	0.947		
	3.11×10^{-3}	1.27		
	3.89×10^{-3}	1.59		

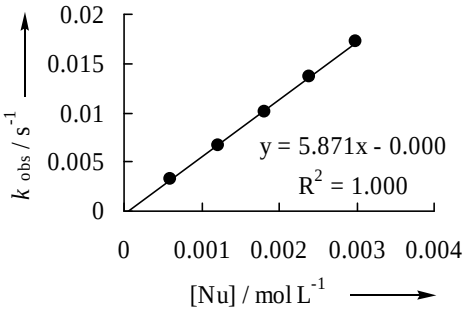
Reactivity parameters for 2,5-dimethylbenzimidazole (2e) in DMSO

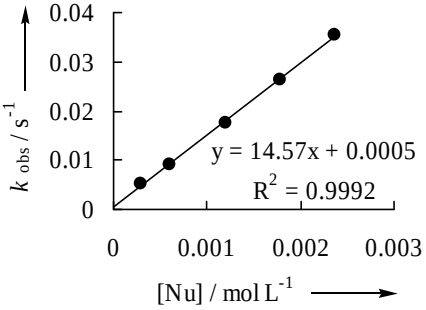
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(jul)_2CH^+$	–9.45	4.53
$(ind)_2CH^+$	–8.76	1.45×10^1
$(thq)_2CH^+$	–8.22	4.75×10^1
$(pyr)_2CH^+$	–7.69	2.00×10^2
$(dma)_2CH^+$	–7.02	4.12×10^2

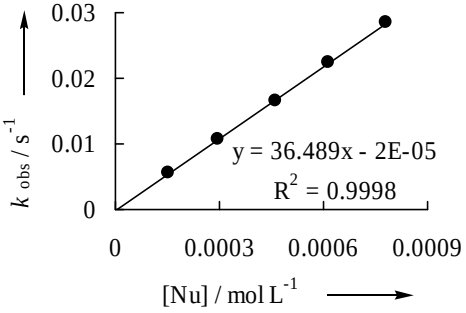


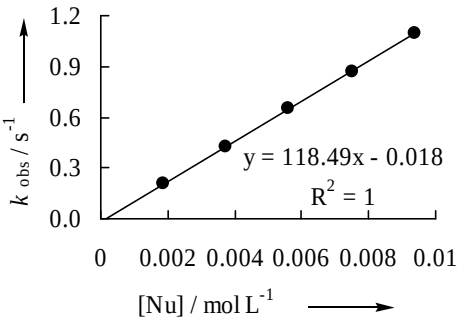
N = 10.21
s = 0.85

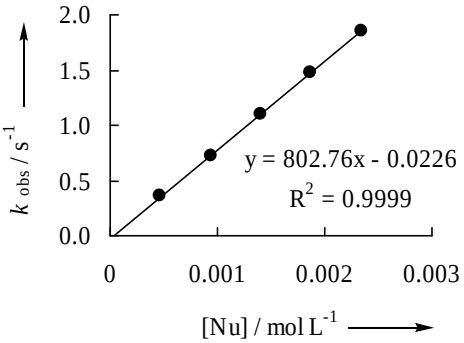
Kinetics of the reactions of 5,6-dimethylbenzimidazole (**2f**) with $(Ar)_2CH^+$ in DMSO at 20°C

$[(lil)_2CH^+]$ (mol L^{-1})	[**2f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 640 nm	k (M^{-1} s^{-1})
1.44×10^{-5}	6.06×10^{-4}	3.27×10^{-3}		5.87
1.44×10^{-5}	1.21×10^{-3}	6.65×10^{-3}		
1.43×10^{-5}	1.80×10^{-3}	1.01×10^{-2}		
1.42×10^{-5}	2.39×10^{-3}	1.36×10^{-2}		
1.42×10^{-5}	2.98×10^{-3}	1.72×10^{-2}		

$[(jul)_2CH^+]$ (mol L^{-1})	[**2f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 645 nm	k (M^{-1} s^{-1})
2.06×10^{-5}	2.96×10^{-4}	5.12×10^{-3}		14.6
2.07×10^{-5}	5.95×10^{-4}	9.13×10^{-3}		
2.08×10^{-5}	1.20×10^{-3}	1.75×10^{-2}		
2.07×10^{-5}	1.78×10^{-3}	2.63×10^{-2}		
2.06×10^{-5}	2.37×10^{-3}	3.53×10^{-2}		

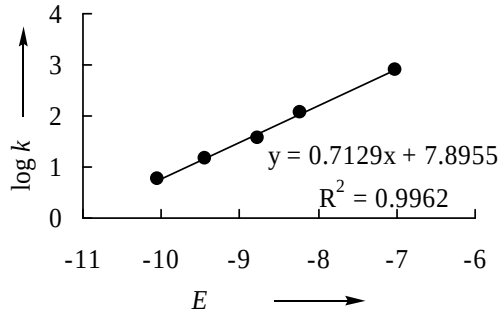
$[(ind)_2CH^+]$ (mol L^{-1})	[**2f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.46×10^{-5}	1.53×10^{-4}	5.68×10^{-3}		36.5
1.40×10^{-5}	2.94×10^{-4}	1.07×10^{-2}		
1.47×10^{-5}	4.63×10^{-4}	1.67×10^{-2}		
1.47×10^{-5}	6.14×10^{-4}	2.24×10^{-2}		
1.49×10^{-5}	7.79×10^{-4}	2.85×10^{-2}		

$[(thq)_2CH^+]$ (mol L^{-1})	[**2f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 618 nm	k (M^{-1} s^{-1})
7.14×10^{-4}	1.87×10^{-3}	0.203		1.18×10^2
	3.75×10^{-3}	0.427		
	5.62×10^{-3}	0.648		
	7.50×10^{-3}	0.869		
	9.37×10^{-3}	1.09		

$[(dma)_2CH^+]$ (mol L^{-1})	[**2f**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 613 nm	k (M^{-1} s^{-1})
3.29×10^{-5}	4.69×10^{-4}	0.360		8.03×10^2
	9.37×10^{-4}	0.727		
	1.41×10^{-3}	1.10		
	1.87×10^{-3}	1.48		
	2.34×10^{-3}	1.86		

Reactivity parameters for 5,6-dimethylbenzimidazole (2f) in DMSO

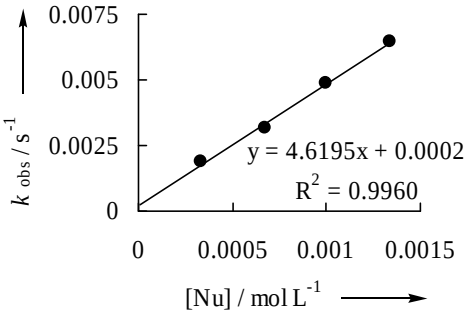
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	5.87
$(jul)_2CH^+$	–9.45	1.46×10^1
$(ind)_2CH^+$	–8.76	3.65×10^1
$(thq)_2CH^+$	–8.22	1.18×10^2
$(dma)_2CH^+$	–7.02	8.01×10^2



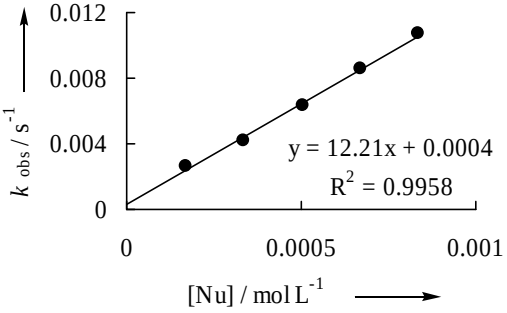
N = 11.08
s = 0.71

Kinetics of the reactions of 5-methoxybenzimidazole (**2g**) with $(Ar)_2CH^+$ in DMSO at 20°C

$[(lil)_2CH^+]$ (mol L^{-1})	[**2g**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 640 nm	k (M^{-1} s^{-1})
1.67×10^{-5}	3.35×10^{-4}	1.87×10^{-3}		4.62
1.68×10^{-5}	6.75×10^{-4}	3.15×10^{-3}		
1.66×10^{-5}	9.97×10^{-4}	4.85×10^{-3}		
1.67×10^{-5}	1.34×10^{-3}	6.44×10^{-3}		

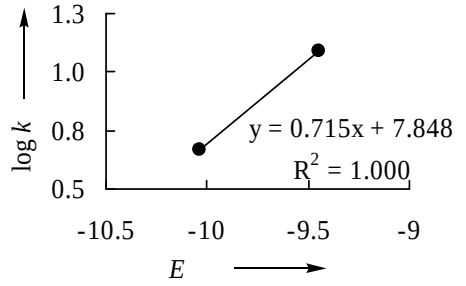


$[(jul)_2CH^+]$ (mol L^{-1})	[**2g**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 645 nm	k (M^{-1} s^{-1})
1.51×10^{-5}	1.69×10^{-4}	2.68×10^{-3}		12.2
1.51×10^{-5}	3.36×10^{-4}	4.22×10^{-3}		
1.51×10^{-5}	5.04×10^{-4}	6.33×10^{-3}		
1.50×10^{-5}	6.70×10^{-4}	8.56×10^{-3}		
1.50×10^{-5}	8.36×10^{-4}	1.07×10^{-2}		



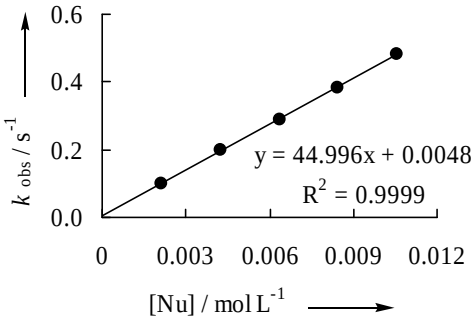
Reactivity parameters for 5-methoxybenzimidazole (2g) in DMSO

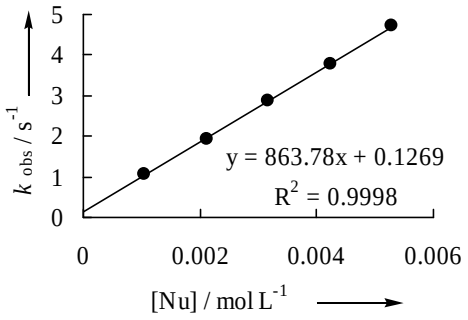
Ar_2CH^+	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	4.62
$(jul)_2CH^+$	–9.45	12.21



***N* = 11.0**
***s* = 0.71**

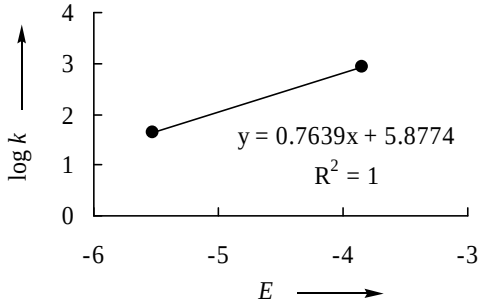
Kinetics of the reactions of benzotriazole (**3a**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

$[(mor)_2CH^+]$ (mol L^{-1})	[**3a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 613 nm	k (M^{-1} s^{-1})
3.29×10^{-5}	2.12×10^{-3}	0.100		45.0
	4.23×10^{-3}	0.196		
	6.35×10^{-3}	0.289		
	8.46×10^{-3}	0.385		
	1.06×10^{-2}	0.482		

$[(mfa)_2CH^+]$ (mol L^{-1})	[**3a**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 586 nm	k (M^{-1} s^{-1})
1.14×10^{-5}	1.06×10^{-3}	1.06		8.64×10^2
	2.12×10^{-3}	1.93		
	3.17×10^{-3}	2.86		
	4.23×10^{-3}	3.77		
	5.29×10^{-3}	4.71		

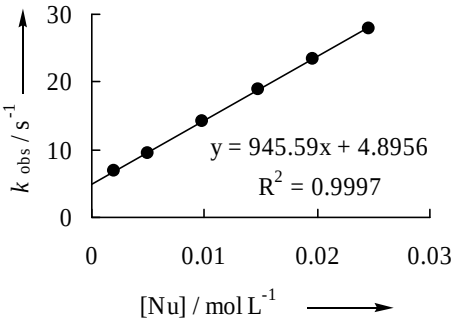
Reactivity parameters for benzotriazole (3a) in CH_3CN

Ar_2CH^+	E	k (M^{-1} s^{-1})
$(mor)_2CH^+$	–5.53	4.50×10^1
$(mfa)_2CH^+$	–3.85	8.64×10^2



***N* = 7.69**
***s* = 0.76**

Kinetics of the reactions of 1-methylbenzotriazole (**3b**) with $(Ar)_2CH^+$ in CH_3CN at 20°C

$[(mfa)_2CH^+]$ (mol L^{-1})	[**3b**] (mol L^{-1})	k_{obs} (s^{-1})	λ = 586 nm	k (M^{-1} s^{-1})
1.12×10^{-5}	1.96×10^{-3}	6.78		9.46×10^{2}
	4.91×10^{-3}	9.37		
	9.81×10^{-3}	14.2		
	1.47×10^{-2}	19.0		
	1.96×10^{-2}	23.5		
	2.45×10^{-2}	28.0		

Reactivity parameters for 1-methylbenzotriazole (3b) in CH_3CN

As only one rate constant is available for 1-methylbenzotriazole (**3b**), its *N* parameter was calculated assuming ***s* = 0.76** as for benzotriazole (**3a**). Thus, log (9.46×10^2) = 0.76(*N* –3.85) and ***N* = 7.77**.

Kinetics for the reactions of imidazoles 1 with benzhydrylium ions in H_2O at 20 °C

When an amine is dissolved in water, the concentration of hydroxide ion increases by protolysis. For that reason, competing reactions of the carbocations with hydroxide and water have to be considered because the observed pseudo-first-order rate constant reflects the sum of the reactions of the electrophile with free amine **1** ($k_{1\Psi,N}$), with OH^- ($k_{1\Psi,OH}$), with water (k_w) and the back reaction ($k_{\leftarrow}$). Rearrangement of eq 1 yields eq 2 where $k_{1\Psi}$ is defined as the overall rate constant minus the contribution of hydroxide.

$$k_{obs} = k_{1\Psi,N} + k_{1\Psi,OH} + k_w + k_{\leftarrow} = k\,[\mathbf{1}]_{effective} + k_{OH}\,[OH^-] + k_w + k_{\leftarrow} \quad (1)$$

$$k_{obs} - k_{OH}[OH^-] = k\,[\mathbf{1}]_{effective} + k_w + k_{\leftarrow} = k_{1\Psi} \quad (2)$$

Concentrations of free amines $[amine]_{effective}$ and of hydroxide ions $[OH^-]$ were calculated from the known pK_B of the amines[S3] as shown below (eq A to F). Combining calculated $[OH^-]$ with published k_{OH} values yielded $k_{1\Psi,OH}$.[S4] Thus, second-order rate constants k for the reactions of imidazoles with benzhydrylium ions in water could be derived from the slopes of the $k_{1\Psi}$ (= $k_{obs} - k_{OH}[OH^-]$) *vs.* $[\mathbf{1}]_{effective}$ plots.

$$R_3N + H_2O \rightleftharpoons R_3NH^+ + OH^- \quad (A)$$

$$K_B = \frac{[\text{ammonium}]\,[OH^-]}{[\text{amine}]_{effective}} \quad (B)$$

$$[\text{amine}]_0 = [\text{amine}]_{effective} + [\text{ammonium}] = [\text{amine}]_{effective} + [OH^-] \quad (C)$$

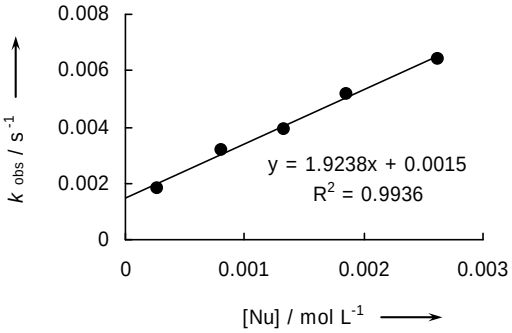
Combination of equation B and C yields $K_B = \frac{[OH^-]^2}{[\text{amine}]_0 - [OH^-]}$ (D)

Solving of the quadratic equation (D) leads to one logic solution for $[OH^-]$ with the "+" in the numerator (eq F).

$$[OH^-] = -\frac{K_B}{2} + \sqrt{\left(\frac{K_B}{2}\right)^2 + K_B[\text{amine}]_0} \quad (F)$$

However, pK_{aH} of imidazoles **1** in H_2O are close to 7 and, therefore, one will not expect formation of considerable amounts of hydroxide ions and protonated imidazoles during kinetic experiments. As shown below, the second-order rate constants for the reactions of 2-methylimidazole (**1d**) with $(ind)_2CH^+$ were determined with and without considering the contribution of hydroxide ions. Both methods yielded identical second-order rate constants. The reactions of benzhydrylium ions with water are very slow compared to the corresponding reactions with imidazoles and, thus, do not affect our kinetic evaluations. Hence the second-order rate constants for the reactions of **1a-b**,**d** with benzhydrylium ions in water were determined without considering the contribution from hydroxide ions and water following the procedure as described for acetonitrile and DMSO solvents. Imidazoles **1** are usually used in high excess to achieve pseudo-first-order conditions and k_{obs} were obtained by fitting the decays of the benzhydrylium absorbances to mono-exponential functions as discussed before.

Determination of second-order rate constants for the reaction of 2-methylimidazole (**1d**) with $(ind)_2CH^+BF_4^-$ in H_2O without considering contribution from OH^- (at 20 °C, cosolvent: 0.2 vol-% CH_3CN):

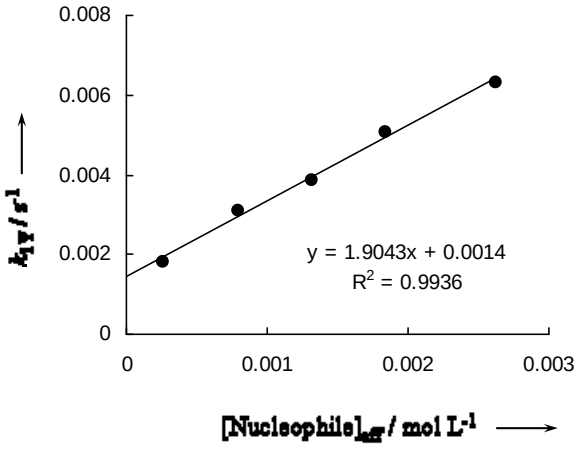
$[(ind)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1d}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
1.90×10^{-5}	2.63×10^{-3}	6.41×10^{-3}		1.92
1.91×10^{-5}	1.85×10^{-3}	5.16×10^{-3}		
1.92×10^{-5}	1.33×10^{-3}	3.93×10^{-3}		
1.93×10^{-5}	8.01×10^{-4}	3.15×10^{-3}		
1.94×10^{-5}	2.69×10^{-4}	1.84×10^{-3}		

Determination of second-order rate constants for the reaction of 2-methylimidazole (**1d**) with $(ind)_2CH^+BF_4^-$ in H_2O considering the contribution from OH^- (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 614 nm):

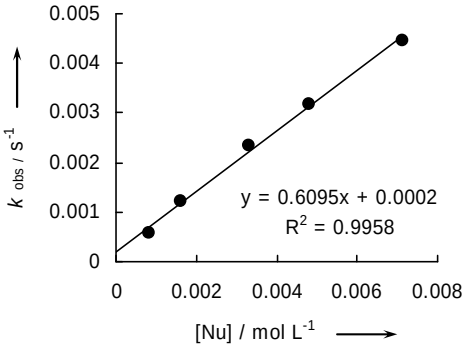
No.	$[(ind)_2CH^+]_0$ (mol L^{-1})	$[Nu]_0$ (mol L^{-1})	$[Nu]_{eff}$ (mol L^{-1})	$[OH^-]$ (mol L^{-1})	$[Nu]_{eff}/[El]_0$	k_{obs} (s^{-1})	$k_{1\Psi,\,OH}$ (s^{-1})	$k_{1\Psi}$ (s^{-1})
ccy70.1	1.90×10^{-5}	2.63×10^{-3}	2.62×10^{-3}	8.50×10^{-6}	138	6.41×10^{-3}	9.18×10^{-5}	6.32×10^{-3}
ccy70.2	1.91×10^{-5}	1.85×10^{-3}	1.84×10^{-3}	7.12×10^{-6}	96	5.16×10^{-3}	7.69×10^{-5}	5.08×10^{-3}
ccy70.3	1.92×10^{-5}	1.33×10^{-3}	1.32×10^{-3}	6.04×10^{-6}	69	3.93×10^{-3}	6.52×10^{-5}	3.86×10^{-3}
ccy70.4	1.93×10^{-5}	8.01×10^{-4}	7.96×10^{-4}	4.68×10^{-6}	41	3.15×10^{-3}	5.06×10^{-5}	3.10×10^{-3}
ccy70.5	1.94×10^{-5}	2.69×10^{-4}	2.66×10^{-4}	2.71×10^{-6}	14	1.84×10^{-3}	2.92×10^{-5}	1.81×10^{-3}

$k = 1.90\ M^{-1}s^{-1}$

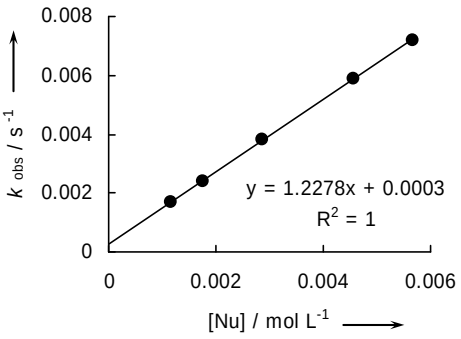
$k_{OH} = 10.8\ M^{-1}s^{-1}$
$pK_B = 7.56$



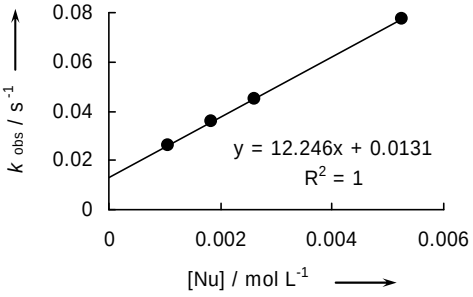
Reaction of imidazole (**1a**) with $(lil)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.4 vol-% CH_3CN)

$[(lil)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1a}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 630 nm	k (M^{-1} s^{-1})
1.91×10^{-5}	7.14×10^{-3}	4.46×10^{-3}		6.10×10^{-1}
1.93×10^{-5}	4.81×10^{-3}	3.17×10^{-3}		
1.99×10^{-5}	3.31×10^{-3}	2.34×10^{-3}		
1.96×10^{-5}	1.63×10^{-3}	1.21×10^{-3}		
1.96×10^{-5}	8.12×10^{-4}	5.75×10^{-4}		

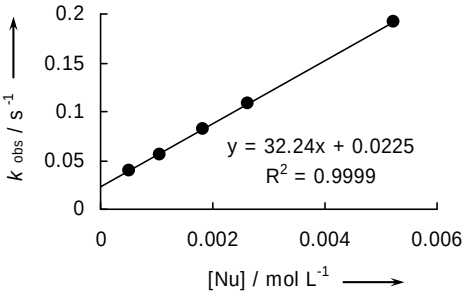
Reaction of imidazole (**1a**) with $(jul)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.2 vol-% CH_3CN)

$[(jul)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1a}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 634 nm	k (M^{-1} s^{-1})
2.58×10^{-5}	5.67×10^{-3}	7.21×10^{-3}		1.23
2.60×10^{-5}	4.56×10^{-3}	5.87×10^{-3}		
2.63×10^{-5}	2.88×10^{-3}	3.82×10^{-3}		
2.66×10^{-5}	1.75×10^{-3}	2.40×10^{-3}		
2.66×10^{-5}	1.16×10^{-3}	1.68×10^{-3}		

Reaction of imidazole (**1a**) with $(pyr)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.2 vol-% CH_3CN)

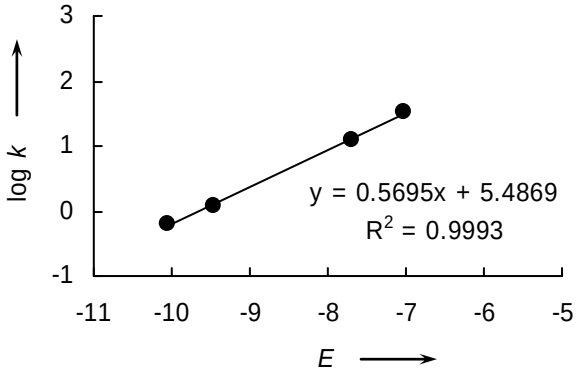
$[(pyr)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1a}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
2.66×10^{-5}	5.24×10^{-3}	7.72×10^{-2}		1.22×10^{1}
2.66×10^{-5}	2.62×10^{-3}	4.52×10^{-2}		
2.66×10^{-5}	1.83×10^{-3}	3.56×10^{-2}		
2.66×10^{-5}	1.05×10^{-3}	2.58×10^{-2}		

Reaction of imidazole (**1a**) with $(dma)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.5 vol-% CH_3CN)

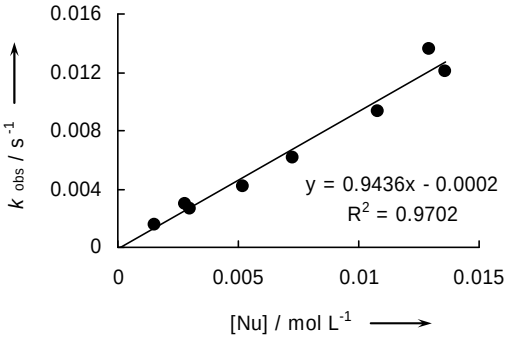
$[(dma)_2CH^+]_0$ (mol L^{-1})	$[Nu]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
1.05×10^{-4}	5.24×10^{-3}	0.191		3.22×10^{1}
1.05×10^{-4}	2.62×10^{-3}	0.108		
1.05×10^{-4}	1.83×10^{-3}	8.19×10^{-2}		
1.05×10^{-4}	1.05×10^{-3}	5.60×10^{-2}		
1.05×10^{-4}	5.24×10^{-4}	3.90×10^{-2}		

Reactivity parameters for imidazole (1a) in H_2O

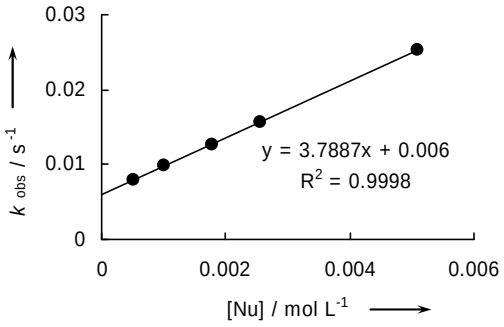
Ar_2CH^+	E	k (M^{-1} s^{-1})	
$(lil)_2CH^+$	-10.04	6.10×10^{-1}	***N* = 9.63**
$(jul)_2CH^+$	-9.45	1.23	***s* = 0.57**
$(pyr)_2CH^+$	-7.69	1.22×10^{1}	
$(dma)_2CH^+$	-7.02	3.22×10^{1}	



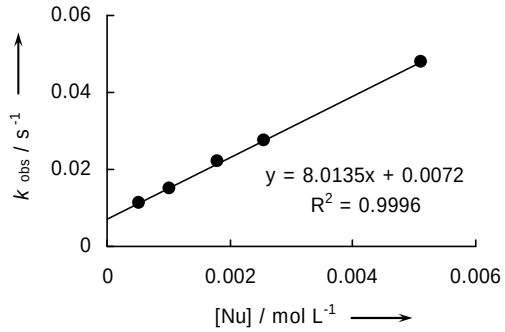
Reaction of 1-methylimidazole (**1b**) with $(lil)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.4 vol-% CH_3CN)

$[(lil)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1b}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 630 nm	k (M^{-1} s^{-1})
1.84×10^{-5}	1.29×10^{-2}	1.36×10^{-2}		9.44×10^{-1}
3.33×10^{-5}	1.36×10^{-2}	1.21×10^{-2}		
3.51×10^{-5}	1.08×10^{-2}	9.35×10^{-3}		
3.55×10^{-5}	7.26×10^{-3}	6.09×10^{-3}		
3.61×10^{-5}	5.18×10^{-3}	4.15×10^{-3}		
1.97×10^{-5}	2.77×10^{-3}	3.01×10^{-3}		
3.63×10^{-5}	2.97×10^{-3}	2.65×10^{-3}		
3.68×10^{-5}	1.51×10^{-3}	1.54×10^{-3}		

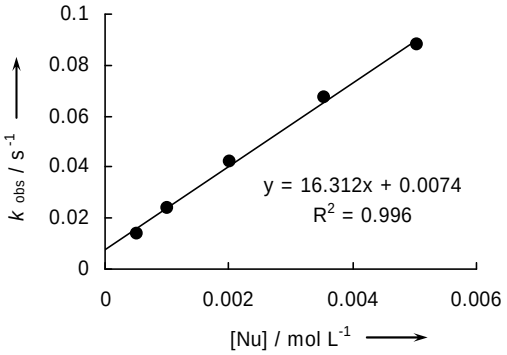
Reaction of 1-methylimidazole (**1b**) with $(ind)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.2 vol-% CH_3CN)

$[(ind)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1b}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.48×10^{-5}	5.10×10^{-3}	2.53×10^{-2}		3.79
1.48×10^{-5}	2.56×10^{-3}	1.57×10^{-2}		
1.48×10^{-5}	1.79×10^{-3}	1.26×10^{-2}		
1.48×10^{-5}	1.02×10^{-3}	9.80×10^{-3}		
1.48×10^{-5}	5.12×10^{-4}	7.99×10^{-3}		

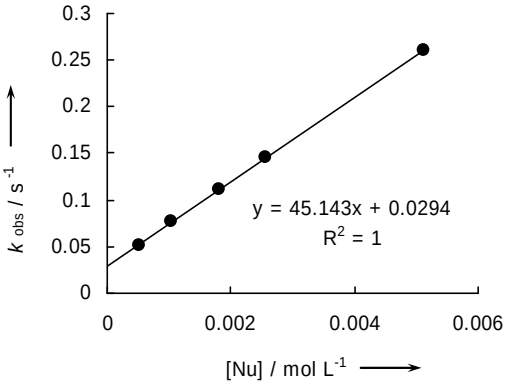
Reaction of 1-methylimidazole (**1b**) with $(thq)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 1.0 vol-% CH_3CN)

$[(thq)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1b}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
3.70×10^{-5}	5.10×10^{-3}	4.81×10^{-2}		8.01
3.70×10^{-5}	2.56×10^{-3}	2.74×10^{-2}		
3.70×10^{-5}	1.79×10^{-3}	2.20×10^{-2}		
3.70×10^{-5}	1.02×10^{-3}	1.52×10^{-2}		
3.70×10^{-5}	5.12×10^{-4}	1.13×10^{-2}		

Reaction of 1-methylimidazole (**1b**) with $(pyr)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.5 vol-% CH_3CN)

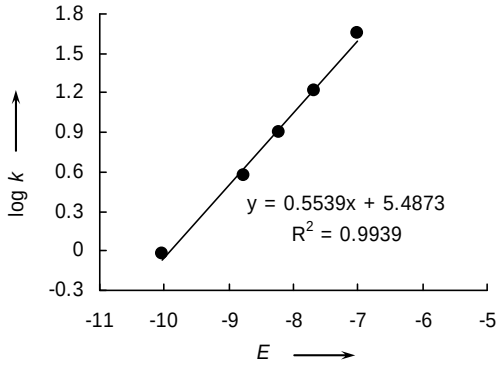
$[(pyr)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1b}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 620 nm	k (M^{-1} s^{-1})
1.79×10^{-5}	5.05×10^{-3}	8.78×10^{-2}		1.63×10^{1}
1.79×10^{-5}	3.54×10^{-3}	6.73×10^{-2}		
1.79×10^{-5}	2.02×10^{-3}	4.21×10^{-2}		
1.79×10^{-5}	1.01×10^{-3}	2.39×10^{-2}		
1.79×10^{-5}	5.05×10^{-4}	1.38×10^{-2}		

Reaction of 1-methylimidazole (**1b**) with $(dma)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.5 vol-% CH_3CN)

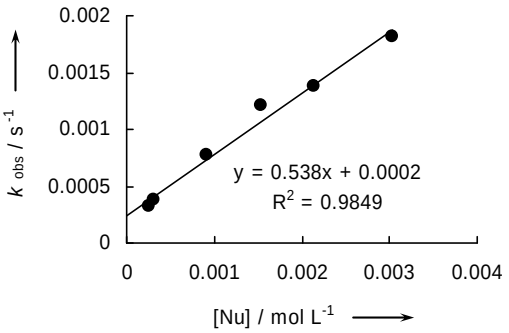
$[(dma)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1b}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
6.70×10^{-5}	5.13×10^{-3}	2.61×10^{-1}		4.51×10^{1}
6.70×10^{-5}	2.57×10^{-3}	1.45×10^{-1}		
6.70×10^{-5}	1.80×10^{-3}	1.11×10^{-1}		
6.70×10^{-5}	1.03×10^{-3}	7.65×10^{-2}		
6.70×10^{-5}	5.13×10^{-4}	5.20×10^{-2}		

Reactivity parameters for N-methylimidazole (1b) in H_2O

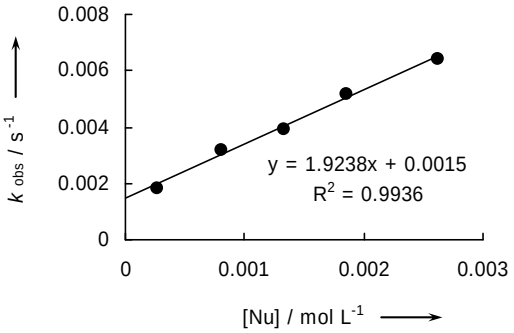
Ar_2CH^+	E	k (M^{-1} s^{-1})	
$(lil)_2CH^+$	-10.04	9.44×10^{-1}	***N* = 9.91**
$(ind)_2CH^+$	-8.76	3.79	***s* = 0.55**
$(thq)_2CH^+$	-8.322	8.01	
$(pyr)_2CH^+$	-7.69	1.63×10^{1}	
$(dma)_2CH^+$	-7.02	4.51×10^{1}	



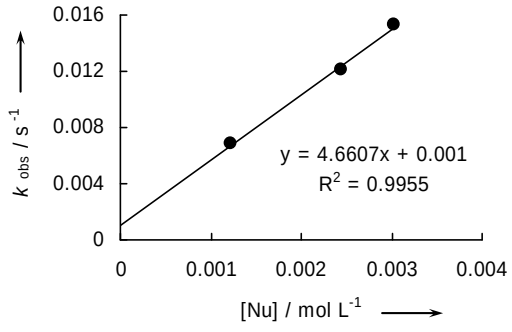
Reaction of 2-methylimidazole (**1d**) with $(lil)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.4 vol-% CH_3CN)

$[(lil)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1d}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 630 nm	k (M^{-1} s^{-1})
2.29×10^{-5}	3.03×10^{-3}	1.82×10^{-3}		5.38×10^{-1}
2.31×10^{-5}	2.14×10^{-3}	1.38×10^{-3}		
2.32×10^{-5}	1.54×10^{-3}	1.21×10^{-3}		
2.31×10^{-5}	9.20×10^{-4}	7.69×10^{-4}		
2.33×10^{-5}	3.09×10^{-4}	3.75×10^{-4}		
1.76×10^{-5}	2.48×10^{-4}	3.29×10^{-4}		

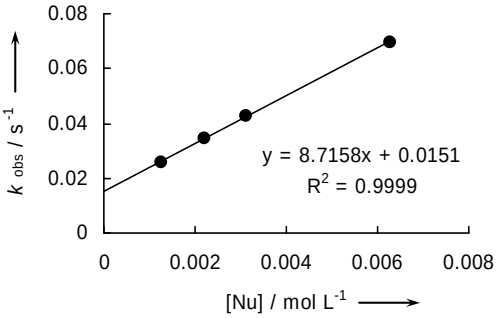
Reaction of 2-methylimidazole (**1d**) with $(ind)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.2 vol-% CH_3CN)

$[(ind)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1d}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 614 nm	k (M^{-1} s^{-1})
1.90×10^{-5}	2.63×10^{-3}	6.41×10^{-3}		1.92
1.91×10^{-5}	1.85×10^{-3}	5.16×10^{-3}		
1.92×10^{-5}	1.33×10^{-3}	3.93×10^{-3}		
1.93×10^{-5}	8.01×10^{-4}	3.15×10^{-3}		
1.94×10^{-5}	2.69×10^{-4}	1.84×10^{-3}		

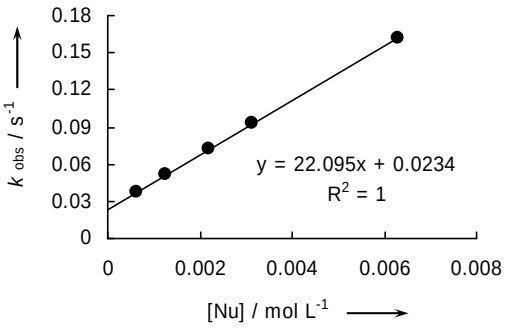
Reaction of 2-methylimidazole (**1d**) with $(thq)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.4 vol-% CH_3CN)

$[(thq)_2CH^+]_0$ (mol L^{-1})	$[\mathbf{1d}]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 618 nm	k (M^{-1} s^{-1})
3.05×10^{-5}	3.02×10^{-3}	1.53×10^{-2}		4.66
3.08×10^{-5}	2.44×10^{-3}	1.17×10^{-2}		
3.09×10^{-5}	2.45×10^{-3}	1.21×10^{-2}		
3.10×10^{-5}	1.23×10^{-3}	6.84×10^{-3}		

Reaction of 2-methylimidazole with $(pyr)_2CH^+BF_4^-$ in H_2O (at 20 °C, cosolvent: 0.2 vol-% CH_3CN)

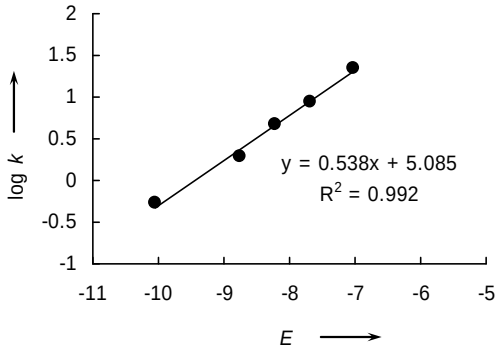
$[(pyr)_2CH^+]_0$ (mol L^{-1})	$[Nu]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
2.66×10^{-5}	6.28×10^{-3}	6.97×10^{-2}		8.72
2.66×10^{-5}	3.14×10^{-3}	4.27×10^{-2}		
2.66×10^{-5}	2.20×10^{-3}	3.42×10^{-2}		
2.66×10^{-5}	1.26×10^{-3}	2.59×10^{-2}		

Reaction of 2-methylimidazole with $(dma)_2CH^+BF_4^-$ (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ (mol L^{-1})	$[Nu]_0$ (mol L^{-1})	k_{obs} (s^{-1})	λ = 610 nm	k (M^{-1} s^{-1})
1.05×10^{-4}	6.28×10^{-3}	1.62×10^{-1}		2.21×10^{1}
1.05×10^{-4}	3.14×10^{-3}	9.31×10^{-2}		
1.05×10^{-4}	2.20×10^{-3}	7.20×10^{-2}		
1.05×10^{-4}	1.26×10^{-3}	5.12×10^{-2}		
1.05×10^{-4}	6.28×10^{-4}	3.71×10^{-2}		

Reactivity parameters for 2-methylimidazole (1d) in H_2O

Ar_2CH^+	E	k (M^{-1} s^{-1})	
$(lil)_2CH^+$	-10.04	5.38×10^{-1}	***N* = 9.45**
$(ind)_2CH^+$	-8.76	1.92	***s* = 0.54**
$(thq)_2CH^+$	-8.322	4.60	
$(pyr)_2CH^+$	-7.69	8.72	
$(dma)_2CH^+$	-7.02	2.21×10^{1}	



References

[S1] a) H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov and H. Schimmel, *J. Am. Chem. Soc.*, 2001**, 123**, 9500-9512.

[S2] Partial decomposition of the products was observed during column chromatography with neutral alumina having higher actvity grade. Neutral alumina with lower activity grade is much better for this purpose.

[S3] For **1a**: a) V. P. Vasil´ev, N. K. Grechina and G. A. Zaitseva, *Zh. Obshch. Khim.*, 1983, **53**, 199-203; For **1b**: b) M. L. Bender and B. W. Turnquest, *J. Am. Chem. Soc.*, 1957, **79**, 1656-1662; c) For **1d**: K. I. Skorey, V. Somayaji and R. S. Brown, *J. Am. Chem. Soc.*, 1989, **111**, 1445-1452.

[S4] For reactions with OH^- and H_2O see: S. Minegishi and H. Mayr, *J. Am. Chem. Soc.*, 2003, **125**, 286-295.