Supplementary data

Table 10

Kinetic results for reaction of **4** with pyrrolidine in DMSO at 25°C

[Pyrrolidine]/ mol dm^{-3}]	[Pyrrolidinium perchlorate]/mol dm^{-3}	k_{fast}[a]/ s^{-1}	k_{calc}[b]/ s^{-1}	k_{slow}[c]/ s^{-1}	k_{calc}[d]/ s^{-1}
0.003	-	140	130	-	-
0.004	-	230	220	-	-
0.005	-	350	350	-	-
0.005	0.01	-	-	0.69	0.66
0.010	0.01	-	-	1.02	1.04
0.020	0.01	-	-	1.08	1.12
0.040	0.01	-	-	0.81	0.79
0.10	0.01	-	-	0.31	0.35

a. Colour forming process of 490 nm.

b. Calculated from equation (3) with $K_6 k_{Am}$ 1.4×10^7 dm^6 mol^{-2} s^{-1}.

c. Colour forming reaction at 363 nm.

d. Calculated from equation (7) with k_2 146 dm^3 mol^{-1} s^{-1} and $K_{c,6}$ 40 dm^3 mol^{-1}.

   Combination of the values of $K_{c,6}$ and $K_6 k_{Am}$ gives k_{AmH^+} 4×10^5 dm^3 mol^{-1} s^{-1}.

Supplementary data

<u>Table 11</u>

Results for the reaction of **5** with pyrrolidine in DMSO at 25°C

[Pyrrolidine] /mol dm^{-3}	[Pyrrolidinium perchlorate]/mol dm^{-3}	$k_{fast}{}^{a}$/ s^{-1}	Abs (495 nm)	$K_{c,6}{}^{b}$/ dm^3 mol^{-1}	$k_{slow}{}^{c}$/ 10^{-3} s^{-1}	$k_{calc}{}^{d}$/ 10^{-3} s^{-1}
0.005	-	140	0.72	-	-	-
0.010	-	410	1.03	-	-	-
0.020	-	-	1.18	-	-	-
0.040	0.01	-	0.32	2.4	-	-
0.01	0.01	-	-		0.37	0.33
0.02	0.01	-	-		1.2	1.2
0.04	0.01	-	-		3.8	3.8
0.05	0.01	-	-		5.3	5.2

Note.   The fast reaction is at the limit of measurement by the stopped-flow technique.
The problem is that at low amine concentration the reaction is not expected to give first order kinetics, while at high amine concentration it becomes too fast to measure. In the presence of added salt the rapid reverse reaction makes the equilibrium process immeasurably fast.

a. Colour forming at 498 nm. From equation (3) the data give $K_6 k_{Am}$ 5×10^6 dm^6 mol^{-2} s^{-1}.

b. Calculated from equation (4) as $K_{c,6} = \left(\dfrac{0.32}{1.18 - 0.32} \right) \times \dfrac{0.01}{(0.04)^2}$.

c. Colour forming at 363 nm.

Supplementary data

d. Calculated from equation (8) with $K_2 k_B$ 3.3 dm^6 mol^{-1} s^{-1} and $K_{c,6}$ 2.4 dm^3 mol^{-1}.

Supplementary data

Table 12

Results for the reaction of **5** with piperidine in DMSO at 25°C

[Piperidine]/ mol dm^{-3}	[Piperidinium perchlorate]/mol dm^{-3}	k_{fast}[a]/s^{-1}	Abs (495 nm)	$K_{c,6}$[c]/ dm^3 mol^{-1}
0.01	0	26	-	-
0.02	0	80	-	-
0.04	0	300	-	-
0.05	0	450	1.15	-
0.04	0.01	-[b]	0.22	1.5
0.05	0.01	-[b]	0.35	1.7

a. Colour forming process at 495 nm. From equation (3), data give $K_6 k_{Am}$ 2 × 10^5 dm^6 mol^{-2} s^{-1}.

b. Too fast to measure.

c. Calculated from equation (4), using absorbance data.

Supplementary data

<u>Table 13</u>

Absorbance data for the reaction of **10a** with *n*-butylamine in DMSO at 25°C

$[BuNH_2]$/mol dm^{-3}	$[BuNH_3{}^+ClO_4{}^-]$/mol dm^{-3}	Abs (470 nm)	$K_{6,Bu}$[a]
0.000	0.001	0.010	
0.050	0.001	0.045	0.021
0.100	0.001	0.096	0.014
0.150	0.001	0.179	0.015
0.200	0.001	0.274	0.016
0.300	0.001	0.417	0.015
0.200	0.000	0.650	-
0.300	0.000	0.713	

a. $K_{6,Bu}$ is defined as $\dfrac{[\mathbf{15}].[BuNH_3^+]}{[\mathbf{10a}].[BuNH_2]^2}$ and calculated as $\dfrac{(Abs - 0.010)}{(0.713 - Abs)} \cdot \dfrac{[BuNH_3^+]}{[BuNH_2]^2}$.

Supplementary data

Table 14

Kinetic and equilibrium results for reaction of **5** with pyrrolidine in DMF at 25°C.

[Pyrrolidine]/ mol dm^{-3}	[Pyrrolidinium perchlorate]/mol dm^{-3}	Abs[a] (495 nm)	$K_{c,6}$[b]/ dm^3 mol^{-1}	k_{slow}[c]/ 10^{-4} s^{-1}	k_{calc}[d]/ 10^{-4} s^{-1}
0.03	0.001	0.16	0.17	-	-
0.04	0.001	0.24	0.15	-	-
0.05	0.001	0.33	0.15	-	-
0.10	-	1.2	-	-	-
0.008	0.001	-		0.79	0.73
0.01	0.001	-		1.14	1.13
0.02	0.001	-		4.1	4.3
0.04	0.001	-		14.4	14.8
0.06	0.001	-		27	27
0.10	0.001	-		48	46

a. At completion of rapid colour forming reaction.

b. Calculated as $K_{c,6} = \left(\dfrac{Abs}{1.2 - Abs} \right) \cdot \dfrac{\left[AmH^+ \right]}{\left[Am \right]^2}$.

c. Measured at 360 nm.

d. Calculated from equation (8) with $K_2 k_b$ 1.15 dm^6 mol^{-2} s^{-1} and $K_{c,6}$ 0.15 dm^3 mol^{-1}.

Supplementary data

Table 15

Kinetic results for the reaction of **4** with pyrrolidine in Acetonitrile at 25°C

[Pyrrolidine]/10^{-3} mol dm^{-3}	$k_{slow}{}^{a}/10^{-2}$ s^{-1}	$k_{calc}{}^{b}/$s^{-1}
0.38	1.2	1.1
0.48	1.5	1.6
0.58	2.3	2.1
1.00	4.7	4.8
2.00	12	12
3.00	21	20
4.00	29	29
5.00	37	37

a. Measured at 360 nm.

b. Calculated from equation (6) with $K_2 k_B$ 1.1×10^5 dm^6 mol^{-2} s^{-1}, k_B/k_{-2} 1300
    dm^3 mol^{-1} and $K_{c,6}$ zero.

Supplementary data