Table S1

Kinetic and equilibrium data for reaction of **1a** with aniline[a] in water at 25°C and pH = 7.6.

[**1a**]/ 10^{-3} mol dm^{-3}	[sulfite]/ 10^{-3} mol dm^{-3}	k_{obs}[b]/ 10^{-3} s^{-1}	k_{obs}[sulfite]/ 10^{-6} mol dm^{-3} s^{-1}	ΔAbs[c]	K[d]/ dm^3 mol^{-1}
3.9	2.2	1.48	3.18	0.286	76
6.3	2.7	1.22	3.27	0.412	78
8.0	3.0	1.12	3.42	0.481	78
17	4.4	1.09	4.89	0.709	77
26	5.4	1.12	6.06	0.811	71
44	6.5	1.30	8.41	0.933	68

a. Concentration is 1×10^{-4} mol dm^{-3}.

b. Measured at 250 nm.

c. Change in absorbance accompanying reaction.

d. Calculated as $\Delta Abs/(\Delta Abs_\infty - \Delta Abs).$[**1a**] with ΔAbs_∞ 1.25. A linear plot of k_{obs}[sulfite] versus [**1a**] gives k_f[sulfite] 1.4×10^{-4} s^{-1} and k_r[sulfite] 2.2×10^{-6} mol dm^{-3} s^{-1} leading to K (= k_f/k_r) 64 dm^3 mol^{-1}.

Table S2

Kinetic and equilibrium data for reaction of **1a** with 4-chloroaniline[a] in water at 25°C and pH 8.0.

[**1a**]/ 10^{-3} mol dm^{-3}	[sulfite]/ 10^{-3} mol dm^{-3}	k_{obs}[b]/ 10^{-4} s^{-1}	k_{obs}[sulfite]/ 10^{-6} mol dm^{-3}	ΔAbs[c]	K[d]/ dm^3 mol^{-1}
8.0	3.0	7.30	2.19	0.620	102
17	4.0	7.66	3.37	0.825	88
34	7.0	8.48	5.43	0.988	75
53	8.0	9.27	7.44	1.13	86
71	10.0	9.87	9.67	1.19	89
90	11.0	10.5	11.54	1.20	75

a. Concentration is 1×10^{-4} mol dm^{-3}.

b. Measured at 255 nm.

c. Change in absorbance accompanying reaction.

d. Calculated as $\Delta Abs/(\Delta Abs_{\infty} - \Delta Abs).$[**1a**] with ΔAbs_{∞} 1.38. Values for derived kinetic parameters are in Table 6.

Table S3

Kinetic and equilibrium data for reaction of **1a** with 3-nitroaniline[a] in water at 25°C and pH 8.0.

[**1a**]/ 10^{-3} mol dm^{-3}	[sulfite]/ 10^{-3} mol dm^{-3}	k_{obs}[b]/ 10^{-4} s^{-1}	k_{obs}[sulfite]/ 10^{-6} s^{-1}	ΔAbs	K/ dm^3 mol^{-1}
8.0	3.0	0.88	0.26	0.394	129
17.0	4.0	0.97	0.43	0.521	121
34	7.0	12.0	0.84	0.632	130
53	8.0	13.2	1.06	0.674	126
71	10.0	14.4	1.41	0.693	119
90	11.0	15.3	1.68	0.714	130

a. Concentration is 1×10^{-4} mol dm^{-3}.

b. Measured at 260 nm.

c. Change in Absorbance accompanying reaction.

d. Calculated as $\Delta Abs/(\Delta Abs_\infty - \Delta Abs).$[**1a**] with ΔAbs_∞ 0.78. A linear plot of k_{obs}[sulfite] versus [**1a**] gives k_f[sulfite] 1.8×10^{-5} s^{-1} and k_r[sulfite] 1.35×10^{-7} mol dm^{-3} s^{-1}, leading to K (= k_f/k_r) 133 dm^3 mol^{-1}.

Table S4

Kinetic and equilibrium data for reaction of **1a** with 3-cyanoaniline[a] in water at 25°C and pH 8.0

[**1a**]/ 10^{-3} mol dm^{-3}	[sulfite]/ 10^{-3} mol dm^{-3}	k_{obs}[b]/ 10^{-4} s^{-1}	k_{obs}[sulfite]/ 10^{-6} mol dm^{-3} s^{-1}	ΔAbs[c]	K/ dm^3 mol^{-1}
8.0	3.0	1.40	0.42	0.535	136
17	4.0	1.36	0.55	0.691	121
34	7.0	1.41	0.99	0.838	132
53	10.0	1.46	1.46	0.893	128
71	12.0	1.51	1.81	0.917	120
90	14.0	1.56	2.18	0.932	111

a. Concentration is 1×10^{-4} mol dm^{-3}.

b. Measured at 257 nm.

c. Change in absorbance accompanying reaction.

d. Calculated as $\Delta Abs/(\Delta Abs_\infty - \Delta Abs)$.[**1a**] with ΔAbs_∞ = 1.025. A linear plot of k_{obs}[sulfite] versus [**1a**] gives k_f[sulfite] 2.4×10^{-5} s^{-1} and k_r[sulfite] 2.1×10^{-7} mol dm^{-3} s^{-1} leading to K (= k_f/k_r) 114 dm^3 mol^{-1}.

Table S5

Kinetic data for reaction of **1b** with aniline[a] in water at 25°C and pH = 7.57.

[**1b**]/ 10^{-2} mol dm^{-3}	[sulfite] 10^{-3} mol dm^{-3}	k_{obs}[b]/ 10^{-3} s^{-1}	k_{obs}[sulfite][c]/ 10^{-5} mol dm^{-3} s^{-1}
1.50	6.3	1.27	0.80
2.30	6.3	1.62	1.02
3.28	6.3	1.98	1.25
4.93	6.3	2.62	1.65
6.24	6.3	3.24	2.04

a. Concentration is 1×10^{-4} mol dm^{-3}.

b. Measured at 250 nm.

c. A linear plot of k_{obs}[sulfite] versus [**1b**] gives k_f[sulfite] 2.5×10^{-4} s^{-1} and k_r[sulfite] 4.2×10^{-6} mol dm^{-3} s^{-1} leading to K (= k_f/k_r) 60 dm^3 mol^{-1}.

Table S6

Variation with pH of values of rate and equilibrium constants for reaction of **1a** with 4-methylaniline.

pH	k_f[sulfite]/ 10^{-4} s^{-1}	k_r[sulfite]/ 10^{-6} mol dm^{-3} s^{-1}	K^a(kinetic)/ dm^3 mol^{-1}	K^b(Abs)/ dm^3 mol^{-1}
5.8	9.0	22	41	58
8.0	3.7	6.4	58	60
9.2	1.9	2.8	68	65
10.0	1.4	2.8	51	51

a. $K = k_f[\text{sulfite}]/k_r[\text{sulfite}]$.

b. Calculated from absorbance changes accompanying reaction.

Table S7

Variation with pH of values of rate and equilibrium constants for reaction of **1a** with 3-chloroaniline.

pH	k_f[sulfite]/ 10^{-4} s^{-1}	k_r[sulfite]/ 10^{-6} mol dm^3 s^{-1}	K^a(kinetic)/ dm^3 mol^{-1}	K^b(Abs)/ dm^3 mol^{-1}
4.7	3.5	3.9	88	95
5.8	2.3	2.4	97	90
8.0	0.79	0.84	94	94
9.2	0.26	0.18	92	95
10.0	0.19	0.20	97	84

a. $K = k_f[\text{sulfite}]/k_r[\text{sulfite}]$.

b. Calculated from absorbance changes accompanying reaction.

Table S8

Variation with pH of values of rate and equilibrium constants for reaction of **1a** with 3-nitroaniline

pH	k_f[sulfite]/ 10^{-5} s^{-1}	k_r[sulfite]/ 10^{-7} mol dm^{-3} s^{-1}	K[a](kinetic)/ dm^3 mol^{-1}	K[b](Abs)/ dm^3 mol^{-1}
4.7	9.3	7.4	126	137
5.8	5.7	4.8	120	138
6.0	6.9	5.6	123	125
8.0	1.8	1.35	133	128
9.2	0.60	0.45	134	121

a. $K = k_f[\text{sulfite}]/k_r[\text{sulfite}]$.

b. Calculated from absorbance changes accompanying reaction.

Table S9

Variation with pH of values of rate and equilibrium constants for reaction of **1a** with 3-cyanoaniline.

pH	k_f[sulfite]/ 10^{-5} s^{-1}	k_r[sulfite]/ 10^{-7} mol dm^3 s^{-1}	K^a(kinetic)/ dm^3 mol^{-1}	K^b(Abs)/ dm^3 mol^{-1}
4.7	12.6	9.6	130	120
5.8	9.9	7.7	129	123
8.0	2.4	2.1	115	125
9.2	0.70	0.52	132	122

a. $K = k_f[\text{sulfite}]/k_r[\text{sulfite}]$.

b. Calculated from absorbance changes accompanying reaction.

Table S10

Variation with pH of values of rate and equilibrium constants for reaction of **1b** with aniline.

pH	k_f[sulfite]/ 10^{-4} s^{-1}	k_r[sulfite]/ 10^{-6} mol dm^3 s^{-1}	K^a(kinetic)/ dm^3 mol^{-1}
5.4	7.9	13	60
6.6	3.6	6.0	60
7.6	2.5	4.2	60
8.4	1.4	2.4	58

a. $K = k_f[\text{sulfite}]/k_r[\text{sulfite}]$.

Table S11

Variation with pH of values of rate and equilibrium constants for reaction of **1a** with 4-chloroaniline

pH	k_f[sulfite]/ 10^{-4} s^{-1}	k_r[sulfite]/ 10^{-6} mol dm^{-3} s^{-1}	K[a][kinetic]/ dm^3 mol^{-1}	K[b](Abs)/ dm^3 mol^{-1}
4.7	5.15	8.63	60	86
5.8	4.36	5.48	80	89
6.0	5.11	8.1	63	76
7.0	1.94	2.82	69	81
8.0	1.21	1.49	81	82
9.2	0.46	0.42	110	90
10.0	0.37	0.45	81	67

a. $K = k_f[\text{sulfite}]/k_r[\text{sulfite}]$.

b. Calculated from changes in absorbance accompanying reaction, as in Tables 3 and 4.