

Supporting information

Effect of Amine Nature on Reaction Rate and Mechanism in Nucleophilic Substitution

Reactions of 2,4-Dinitrophenyl X-Substituted Benzenesulfonates with Alicyclic

Secondary Amines

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The k_2/k_{-1} ratios for the reaction of 2,4-dinitrophenyl benzenesulfonate with secondary amines have been determined using eqs S1 - S6. Eq (5) can be simplified to eqs (S1) and (S2). Then, β_1 and β_2 can be expressed as eqs (S3) and (S4), respectively.

$$k_N^{S-O} = k_1 k_2 / (k_{-1} + k_2) \quad (5)$$

$$k_N^{S-O} = k_1 k_2 / k_{-1}, \text{ when } k_2 \ll k_{-1} \quad (S1)$$

$$k_N^{S-O} = k_1, \text{ when } k_2 \gg k_{-1} \quad (S2)$$

$$\beta_1 = d(\log k_1) / d(pK_a) \quad (S3)$$

$$\begin{aligned} \beta_2 &= d(\log k_1 k_2 / k_{-1}) / d(pK_a) \\ &= \beta_1 + d(\log k_2 / k_{-1}) / d(pK_a) \end{aligned} \quad (S4)$$

Eq (S4) can be rearranged as eq (S5). Integral of eq (S5) from pK_a^0 results in eq (S6).

Since $k_2 = k_{-1}$ at pK_a^0 , the term $(\log k_2 / k_{-1})_{pK_a^0}$ is zero. Therefore, one can calculate the k_2/k_{-1} ratio for the reactions of 2,4-dinitrophenyl benzenesulfonate with all the alicyclic secondary amines studied from eq (S6) using $\beta_1 = 0.38$, $\beta_2 = 0.86$, $pK_a^0 = 9.1$.

$$\beta_2 - \beta_1 = d(\log k_2 / k_{-1}) / d(pK_a) \quad (S5)$$

$$(\log k_2 / k_{-1})_{pK_a} = (\beta_2 - \beta_1)(pK_a - pK_a^0) \quad (S6)$$

Table S1. Summary of second-order rate constants for the reaction of 2,4-dinitrophenyl X-substituted benzenesulfonates (**1a-e**) with piperidine in 80 mol % H₂O - 20 mol % DMSO at 25.0±0.1°C.

X	$k_N^{\text{tot}}/\text{M}^{-1}\text{s}^{-1}$	$k_N^{\text{S-O}}/\text{M}^{-1}\text{s}^{-1}$	% ^a
4-NO ₂	49.9±0.5	49.9±0.5	100
4-Cl	15.1±0.3	15.1±0.3	100
H	11.1±0.3	11.1±0.3	100
4-Me	8.20±0.05	8.20±0.05	100
4-MeO	5.30±0.07	5.30±0.07	100

^a % of S-O bond fission.

Table S2. Summary of second-order rate constants for the reaction of 2,4-dinitrophenyl X-substituted benzenesulfonates (**1a-e**) with piperazinium ion in 80 mol % H₂O - 20 mol % DMSO at 25.0±0.1°C.

X	$10^3 k_N^{\text{tot}}/\text{M}^{-1}\text{s}^{-1}$	$10^3 k_N^{\text{S-O}}/\text{M}^{-1}\text{s}^{-1}$	$10^3 k_N^{\text{C-O}}/\text{M}^{-1}\text{s}^{-1}$	% ^a
4-NO ₂	45.5±0.6	35.5	10.0	78
4-Cl	21.7±0.6	16.5	5.20	76
H	18.1±0.3	11.9	6.20	66
4-Me	13.0±0.8	8.84	4.16	68
4-MeO	10.3±0.2	6.70	3.60	65

^a % of S-O bond fission.

Table S3. Kinetic data for the reaction of 2,4-dinitrophenyl benzenesulfonate (**1c**) with piperidine in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ³ s ⁻¹
1	1.53	17.5
2	2.28	26.9
3	3.03	35.3
4	3.78	43.4
5	4.51	50.7

$$k_N^{\text{tot}} = 11.1 \pm 0.3 \text{ M}^{-1}\text{s}^{-1}$$

corr. coeff. =0.9991

Table S4. Kinetic data for the reaction of 2,4-dinitrophenyl benzenesulfonate (**1c**) with 3-methylpiperidine in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ³ s ⁻¹
1	1.59	16.8
2	2.38	24.7
3	3.16	33.0
4	3.93	41.1
5	4.70	49.4

$k_N^{\text{tot}} = 10.5 \pm 0.1 \text{ M}^{-1}\text{s}^{-1}$

corr. coeff. = 0.9999

Table S5. Kinetic data for the reaction of 2,4-dinitrophenyl benzenesulfonate (**1c**) with piperazine in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} /10 ⁻³ s ⁻¹
1	1.57	7.27
2	3.11	15.1
3	4.63	23.3
4	6.13	31.1
5	7.60	38.5

$k_N^{\text{tot}} = 5.20 \pm 0.03 \text{ M}^{-1}\text{s}^{-1}$

corr. coeff. = 0.9999

Table S6. Kinetic data for the reaction of 2,4-dinitrophenyl benzenesulfonate (**1c**) with morpholine in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ⁻³ s ⁻¹
1	4.79	4.83
2	9.36	9.08
3	13.7	13.5
4	17.9	17.7
5	21.8	21.4

$k_N^{\text{tot}} = 0.980 \pm 0.008 \text{ M}^{-1}\text{s}^{-1}$

corr. coeff. = 0.9999

Table S7. Kinetic data for the reaction of 2,4-dinitrophenyl benzenesulfonate (**1c**) with 1-formylpiperazine in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ³ s ⁻¹
1	18.2	4.60
2	33.4	8.66
3	46.3	12.0
4	57.3	14.7
5	66.9	17.4

$k_N^{\text{tot}} = 0.260 \pm 0.003 \text{ M}^{-1}\text{s}^{-1}$

corr. coeff. = 0.9999

Table S8. Kinetic data for the reaction of 2,4-dinitrophenyl benzenesulfonate (**1c**) with piperazinium ion in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ⁻³ s ⁻¹
1	48.6	0.848
2	61.9	1.11
3	73.0	1.30
4	82.3	1.46
5	90.3	1.61

$$k_N^{\text{tot}} = 0.0181 \pm 0.0003 \text{ M}^{-1}\text{s}^{-1}$$

corr. coeff. = 0.9996

Table S9. Kinetic data for the reaction of 2,4-dinitrophenyl 4-nitrobenzenesulfonate (**1a**)

with piperidine in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ⁻³ s ⁻¹
1	1.53	74.6
2	1.91	92.2
3	2.28	110
4	3.03	149
5	3.78	186

$$k_N^{\text{tot}} = 49.9 \pm 0.5 \text{ M}^{-1}\text{s}^{-1}$$

corr. coeff. = 0.9999

Table S10. Kinetic data for the reaction of 2,4-dinitrophenyl 4-chlorobenzenesulfonate (**1b**)

with piperidine in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ³ s ⁻¹
1	1.53	22.1
2	2.28	34.3
3	3.03	45.2
4	3.78	56.4
5	4.51	67.5

$$k_N^{\text{tot}} = 15.1 \pm 0.3 \text{ M}^{-1}\text{s}^{-1}$$

corr. coeff. = 0.9996

Table S11. Kinetic data for the reaction of 2,4-dinitrophenyl 4-methylbenzenesulfonate (**1d**) with piperidine in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ³ s ⁻¹
1	2.28	17.5
2	3.03	23.4
3	3.78	29.6
4	4.51	35.7
5	5.25	41.8

$k_N^{\text{tot}} = 8.20 \pm 0.05 \text{ M}^{-1}\text{s}^{-1}$

corr. coeff. = 0.9999

Table S12. Kinetic data for the reaction of 2,4-dinitrophenyl 4-methoxy-

benzenesulfonate (**1e**) with piperidine in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ⁻³ s ⁻¹
1	2.28	12.8
2	3.03	17.0
3	3.78	20.8
4	4.51	24.9
5	5.25	28.5

$$k_N^{\text{tot}} = 5.30 \pm 0.07 \text{ M}^{-1}\text{s}^{-1}$$

corr. coeff. = 0.9997

Table S13. Kinetic data for the reaction of 2,4-dinitrophenyl 4-nitrobenzenesulfonate (**1a**)

with piperazinium ion in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	<i>k</i> _{obsd} / 10 ⁻³ s ⁻¹
1	50.8	2.31
2	64.6	2.93
3	76.2	3.47
4	86.0	3.91
5	94.4	4.29

$$k_N^{\text{tot}} = 0.0455 \pm 0.0006 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9999$$

Table S14. Kinetic data for the reaction of 2,4-dinitrophenyl 4-chlorobenzenesulfonate (**1b**)

with piperazinium ion in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	<i>k</i> _{obsd} / 10 ⁻³ s ⁻¹
1	50.8	1.09
2	64.6	1.43
3	76.2	1.67
4	86.0	1.88
5	94.4	2.04

$$k_N^{\text{tot}} = 0.0217 \pm 0.0006 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{corr. coeff.} = 0.9989$$

Table S15. Kinetic data for the reaction of 2,4-dinitrophenyl 4-methylbenzenesulfonate (**1d**) with piperazinium ion in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ⁻³ s ⁻¹
1	55.6	0.800
2	67.6	0.938
3	77.8	1.09
4	86.5	1.20
5	94.0	1.29

$$k_N^{\text{tot}} = 0.0130 \pm 0.0008 \text{ M}^{-1}\text{s}^{-1}$$

corr. coeff. = 0.9992

Table S16. Kinetic data for the reaction of 2,4-dinitrophenyl 4-methoxybenzenesulfonate (**1e**) with piperazinium ion in 80 mol % H₂O – 20 mol % DMSO at 25.0±0.1°C.

	[R ₂ NH] / 10 ⁻³ M	k _{obsd} / 10 ⁻³ s ⁻¹
1	55.6	0.504
2	67.6	0.620
3	77.8	0.722
4	86.5	0.811
5	94.0	0.902

$$k_N^{\text{tot}} = 0.0103 \pm 0.0002 \text{ M}^{-1}\text{s}^{-1}$$

corr. coeff. = 0.9992