Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Electronic Supplementary Information

Aminolysis of 4-nitrophenyl phenyl carbonate and thionocarbonate: Effects of amine nature and modification of electrophilic center from C=O to C=S on reactivity and mechanism

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Table S1 Kinetic data for the reaction of 4-nitrophenyl phenyl carbonate (**5**) with piperazinium ion in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-4}s^{-1}$
1	17.3	9.32
2	31.7	17.8
3	44.0	25.1
4	54.4	32.0
5	63.5	38.1

$k_N = (6.22 \pm 0.11) \times 10^{-2}\ M^{-1}s^{-1}$
intercept = $(-1.76 \pm 0.52) \times 10^{-4}\ s^{-1}$
$R^2 = 0.9995$

Table S2 Kinetic data for the reaction of 4-nitrophenyl phenyl carbonate (**5**) with 1-formylpiperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-3}\ s^{-1}$
1	10.6	17.9
2	20.3	33.5
3	29.2	48.4
4	47.0	78.1
5	55.9	93.9

$k_N = 1.68 \pm 0.01\ M^{-1}s^{-1}$
intercept = $(-2.91 \pm 4.71) \times 10^{-4}\ s^{-1}$
$R^2 = 0.9999$

Table S3 Kinetic data for the reaction of 4-nitrophenyl phenyl carbonate (**5**) with morpholine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-2}s^{-1}$
1	10.8	12.3
2	21.6	24.0
3	32.4	36.5
4	43.2	48.5
5	54.0	61.0

$k_N = 11.3 \pm 0.1\ M^{-1}s^{-1}$
intercept = $(-0.11 \pm 0.25) \times 10^{-2}\ s^{-1}$
$R^2 = 0.9999$

Table S4 Kinetic data for the reaction of 4-nitrophenyl phenyl carbonate (**5**) with 1-(2-hydroxyethyl)piperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-1}s^{-1}$
1	11.0	2.89
2	22.0	5.77
3	33.0	8.75
4	44.0	11.7
5	55.0	15.1

$k_N = 27.6 \pm 0.5\ \ M^{-1}s^{-1}$
intercept = $(-2.63 \pm 1.82) \times 10^{-2}\ s^{-1}$
$R^2 = 0.9995$

Table S5 Kinetic data for the reaction of 4-nitrophenyl phenyl carbonate (**5**) with piperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-1}s^{-1}$
1	11.0	11.2
2	21.9	22.7
3	32.9	34.7
4	43.8	45.7
5	54.8	58.8

$k_N = 108 \pm 2\ M^{-1}s^{-1}$
intercept = $(-8.73 \pm 5.48) \times 10^{-2}\ s^{-1}$
$R^2 = 0.9997$

Table S6 Kinetic data for the reaction of 4-nitrophenyl phenyl carbonate (**5**) with 3-methylpiperidine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

	$[R_2NH] / 10^{-3}M$	k_{obsd} / s^{-1}
1	10.5	2.38
2	20.9	4.91
3	31.4	7.43
4	41.8	10.0
5	52.3	12.8

$k_N = 248 \pm 3\ M^{-1}s^{-1}$
intercept = $(-2.83 \pm 1.02) \times 10^{-1}\ s^{-1}$
$R^2 = 0.9997$

Table S7 Kinetic data for the reaction of 4-nitrophenyl phenyl carbonate (**5**) with piperidine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	k_{obsd} / s^{-1}
1	10.9	2.98
2	21.8	5.99
3	32.7	9.24
4	43.6	12.4
5	54.5	15.7

$k_{app} = 292 \pm 3\ M^{-1}s^{-1}$
intercept = $(-2.9 \pm 0.9) \times 10^{-1}\ s^{-1}$
$R^2 = 0.9998$

Table S8 Kinetic data for the reaction of 4-nitrophenyl phenyl thionocarbonate (**6**) with piperazinium ion in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-3}s^{-1}$
1	9.07	1.22
2	17.3	2.74
3	31.8	6.37
4	44.8	11.0
5	54.5	15.6
6	63.6	19.9
7	76.3	27.9

Table S9 Kinetic data for the reaction of 4-nitrophenyl phenyl thionocarbonate (**6**) with 1-formylpiperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-2}s^{-1}$
1	10.6	1.79
2	20.3	4.69
3	29.2	8.22
4	37.3	11.3
5	44.7	14.5
7	51.6	18.2
8	58.0	21.5

Table S10 Kinetic data for the reaction of 4-nitrophenyl phenyl thionocarbonate (**6**) with morpholine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-1}s^{-1}$
1	12.4	0.856
2	20.4	1.52
3	30.6	2.86
4	40.8	3.94
5	51.0	5.30
6	61.2	6.65
7	71.4	7.91
8	81.6	9.07

Table S11 Kinetic data for the reaction of 4-nitrophenyl phenyl thionocarbonate (**6**) with 1-(2-hydroxyethyl) piperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-1}s^{-1}$
1	4.19	0.268
2	8.82	0.615
3	14.0	1.18
4	20.4	1.98
5	30.6	3.41
6	40.8	4.49
7	51.0	6.10

Table S12 Kinetic data for the reaction of 4-nitrophenyl phenyl thionocarbonate (**6**) with piperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-1}s^{-1}$
1	5.50	1.39
2	11.0	3.04
3	22.0	6.68
4	33.0	11.1
5	44.0	14.8
6	55.0	19.5
7	66.0	23.7

Table S13 Kinetic data for the reaction of 4-nitrophenyl phenyl thionocarbonate (**6**) with 3-methylpiperidine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-1}s^{-1}$
1	10.4	3.29
2	20.7	6.92
3	31.1	10.7
4	41.4	14.6
5	51.8	18.7
6	62.1	23.1
7	72.5	28.0

Table S14 Kinetic data for the reaction of 4-nitrophenyl phenyl thionocarbonate (**6**) with piperidine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

	$[R_2NH] / 10^{-3}M$	$k_{obsd} / 10^{-1}s^{-1}$
1	5.45	1.49
2	10.6	2.82
3	21.1	5.71
4	32.7	8.91
5	43.6	13.1
6	54.5	16.3
7	65.4	20.3
8	76.3	24.4

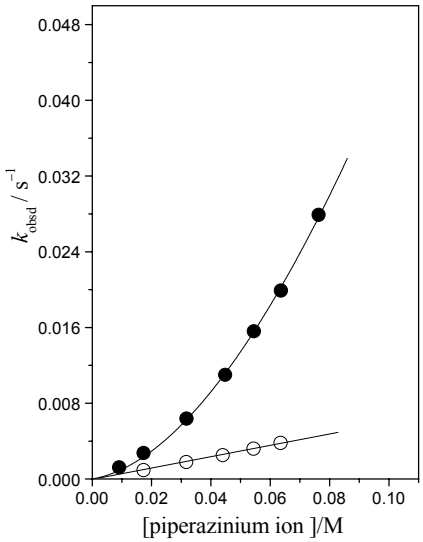


Fig. S1 Plots of k_{obsd} *vs.* amine concentration for reactions of 4-nitrophenyl phenyl carbonate (○) and thionocarbonate (●) with piperazinium ion in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

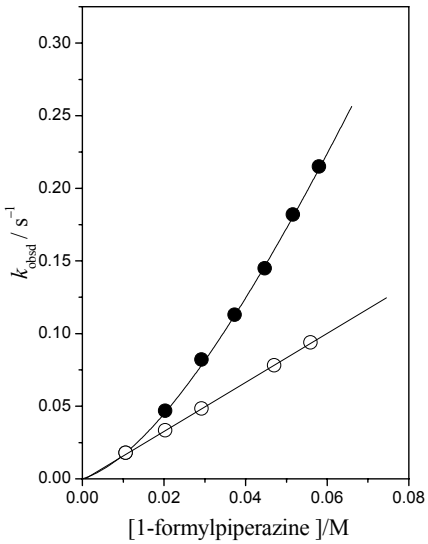


Fig. S2 Plots of k_{obsd} *vs.* amine concentration for reactions of 4-nitrophenyl phenyl carbonate (○) and thionocarbonate (●) with 1-formylpiperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

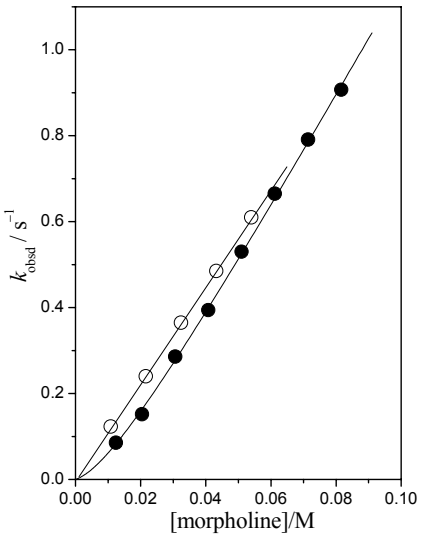


Fig. S3 Plots of k_{obsd} *vs.* amine concentration for reactions of 4-nitrophenyl phenyl carbonate (○) and thionocarbonate (●) with morpholine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

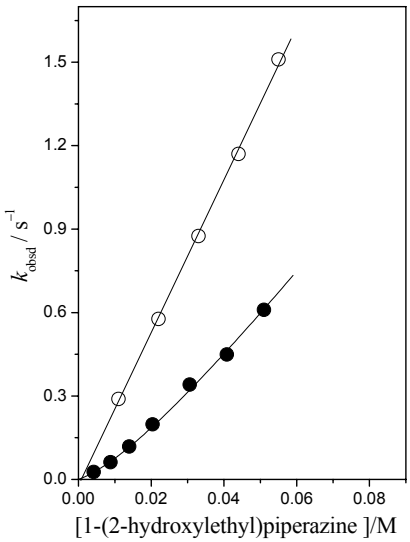


Fig. S4 Plots of k_{obsd} *vs.* amine concentration for reactions of 4-nitrophenyl phenyl carbonate (○) and thionocarbonate (●) with 1-(2-hydroxylethyl)piperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

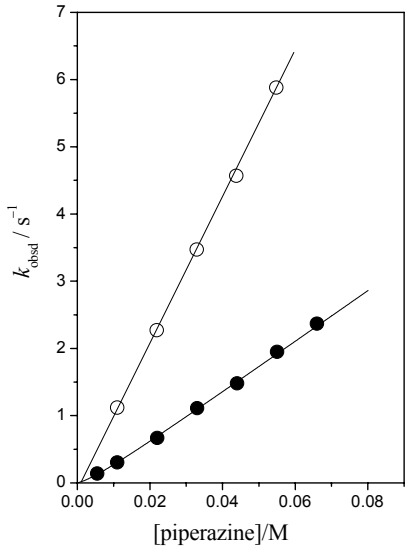
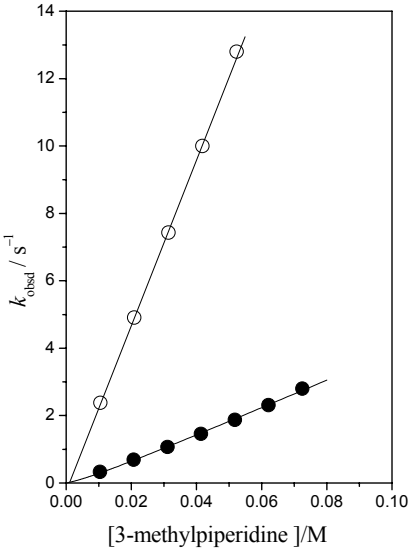


Fig. S5 Plots of k_{obsd} *vs.* amine concentration for reactions of 4-nitrophenyl phenyl carbonate (○) and thionocarbonate (●) with piperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.



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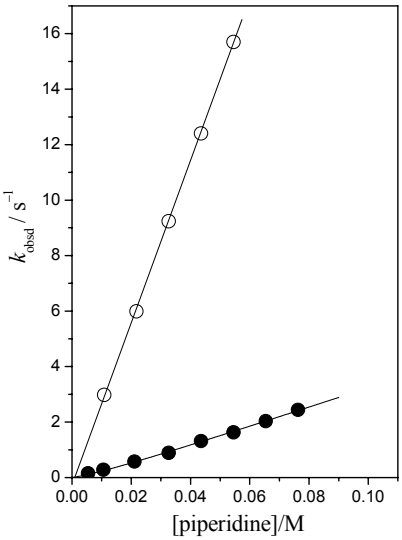

Fig. S7 Plots of k_{obsd} *vs.* amine concentration for reactions of 4-nitrophenyl phenyl carbonate (○) and thionocarbonate (●) with piperidine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

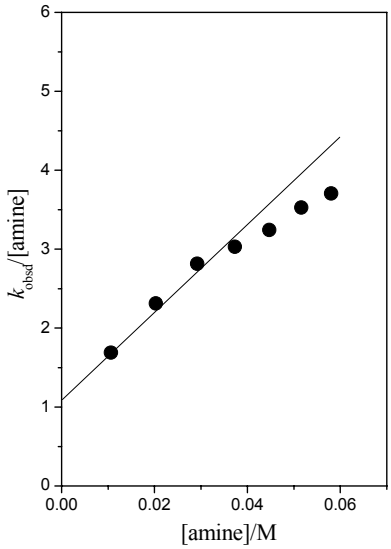

Fig. S8 Plot of k_{obsd}/[amine] *vs.* [amine] for the reaction of 4-nitrophenyl phenyl thionocarbonate (**6**) with 1-formylpiperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

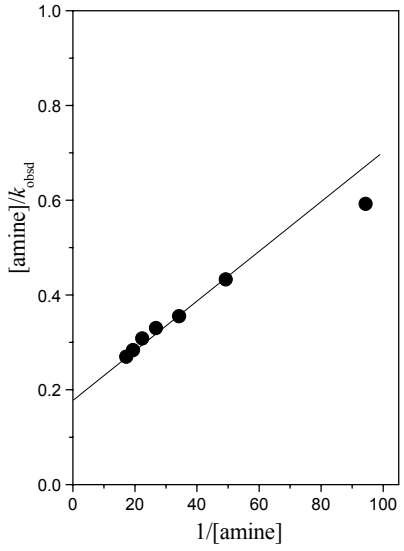

Fig. S9 Plot of [amine]/k_{obsd} *vs.* 1/[amine] for the reaction of 4-nitrophenyl phenyl thionocarbonate (**6**) with 1-formylpiperazine in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 ^oC.

The k_2/k_{-1} ratios for the reaction of 4–nitrophenyl phenyl carbonate (**5**) and secondary amines have been determined using eqns S1 - S6.

Eqn (3) can be simplified to eqns (S1) and (S2). Then, β_1 and β_2 can be expressed as eqns (S3) and (S4), respectively.

$$k_N = k_1k_2/(k_{-1} + k_2) \quad (3)$$

$$k_N = k_1k_2/k_{-1}, \text{ when } k_2 << k_{-1} \quad (S1)$$

$$k_N = k_1, \text{ when } k_2 >> k_{-1} \quad (S2)$$

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

$$\beta_2 = d(\log k_1\, k_2/k_{-1})/d(pK_a)$$

$$= \beta_1 + d(\log k_2/k_{-1})/d(pK_a) \quad (S4)$$

Eqn (S4) can be rearranged as eqn (S5). Integral of eqn (S5) from pK_a^o results in eqn (S6). Since $k_2 = k_{-1}$ at pK_a^o, the term $(\log k_2/k_{-1})_{pKa}{}^o$ is zero. Therefore, one can calculate the k_2/k_{-1} ratio from eqn (S6) using $\beta_1 = 0.26$, $\beta_2 = 0.98$, $pK_a^o = 10.1$ with all the secondary amines.

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

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