SUPPORTING INFORMATION

Kinetic Study of the Aminolysis and Pyridinolysis of *O*-Phenyl and *O*-Ethyl *O*-(2,4-Dinitrophenyl) Thiocarbonates. A Remarkable Leaving Group Effect

Enrique A. Castro, María Cubillos, Margarita Aliaga, Sandra Evangelisti, and José G. Santos

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TABLE S1. Experimental Conditions and k_{obsd} Values for the Reactions of SA Amines with *O*-Phenyl *O*-(2,4-Dinitrophenyl) Thiocarbonate (1)[a]

amine	pH	F_N[b]	$10^2[N]_{tot}$[c] /M	$10^2 k_{obsd}$ /s^{-1}	no. of runs
piperidine	10.94	0.33	0.90–8.2	4.6–19	7
	11.24	0.50	1.0–8.0	5.3–28	8
	11.54	0.67	0.53–5.5	4.2–24	8
piperazine	9.64	0.33	0.031–0.31	0.051-0.58	4
	9.94	0.50	0.031–0.31	0.12–0.97	7
	10.24	0.67	0.031–0.31	0.12–1.3	6
1-(2-hydroxyethyl)piperazine	9.08	0.33	0.036–0.36	0.014–0.32	6
	9.38	0.50	0.058–0.58	0.080–0.80	7
	9.68	0.67	0.074–0.74	0.016–1.4	7
morpholine	8.48	0.33	0.044–0.44	0.17–3.5	6
	8.78	0.50	0.046–0.46	0.055–0.43	6
	9.08	0.67	0.053–0.45	0.065–0.53	6
1–formylpiperazine	7.68	0.33	5.0–15	0.90–3.5	5
	7.98	0.50	2.0–16	0.72–6.1	4
	8.28	0.67	2.2–14	0.82–6.0	6
piperazinium ion	5.51	0.33	1.7–14	0.75–1.2	6
	5.81	0.49	2.3–19	0.85–1.7	6

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Free amine fraction. [c] Concentration of total amine (free base plus protonated forms).

TABLE S2. Experimental Conditions and k_{obsd} Values for the Reactions of SA Amines with *O*-Ethyl *O*-(2,4-Dinitrophenyl) Thiocarbonate (2)[a]

SA amine	pH	F_N [b]	10^2 [N] $]_{tot}$ [c] / M	$10^3 k_{obsd}$ / s^{-1}	no. of runs
piperidine	10.94	0.33	0.050–0.50	2.5–16	7
	11.24	0.50	0.050–0.50	4.1–25	7
	11.54	0.66	0.050–0.50	6.5–32	7
piperazine	9.64	0.33	0.10–1.0	1.6–29	7
	9.94	0.50	0.050–1.0	1.9–37	9
	10.24	0.66	0.10–1.0	5.0–65	7
1-(2-hydroxyethyl)piperazine	9.08	0.33	0.10–1.0	1.3–14	7
	9.38	0.50	0.10–0.85	2.0–19	7
	9.68	0.66	0.10–1.0	1.8–25	7
morpholine	8.48	0.33	0.10–1.0	1.2–12	7
	8.78	0.50	0.10–1.0	1.7–18	7
	9.08	0.66	0.10–1.0	2.0–22	7
1-formylpiperazine	7.68	0.33	7.0–30	34–170	6
	7.98	0.50	0.15–30	0.80–266	15
piperazinium ion	5.50	0.33	1.0–8.5	1.3–9.4	6
	5.80	0.49	1.0–10	1.5–13	7
	6.20	0.71	1.0–10	2.2–21	7

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Free amine fraction. [c] Concentration of total amine (free base plus protonated forms).

TABLE S3. Experimental Conditions and k_{obsd} values for the Pyridinolysis of *O*-Phenyl *O*-(2,4-Dinitrophenyl) Thiocarbonate (1)[a]

pyridine substituent	pH	F_N[b]	10^3 [N]]$_{tot}$[c] / M	$10^3 k_{obsd}$ / s^{-1}	no. of runs
4-(dimethylamino)	8.2	0.021	1.0–10	3.7–33	8
	8.5	0.041	0.75–4.0	6.4–26	5
	8.8	0.078	0.65–4.8	9.2–33	6
4-amino	9.1	0.35	0.20–2.0	2.4–31	6
	9.4	0.52	0.20–2.0	3.4–50	6
	9.7	0.68	0.20–1.7	10–56	7
3,4-dimethyl[d]	8.0	0.94	1.0–10	19–190	7
	8.2	0.96	0.80–8.0	13–140	9
	8.5	0.98	0.80–8.0	15–151	6
4-methyl	6.0	0.36	2.7–15	8.8–34	7
	6.3	0.53	0.80–8.0	4.3–29	6
	6.6	0.69	0.70–7.0	4.7–34	6
3-methyl	5.6	0.36	10–98	15–94	7
	5.9	0.52	8.0–80	15–122	9
	6.2	0.69	10–53	29–98	7
none	5.1	0.35	15–55	5.4–21	6
	5.4	0.52	5.0–40	5.2–23	8
	5.7	0.68	2.6–26	1.7–18	7
3-carbamoyl[d]	8.2	1.0	20–200	0.26–2.8	7
	8.5	1.0	40–190	0.57–2.5	6
	8.8	1.0	30–200	0.40–2.4	5

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Free amine fraction. [c] Concentration of total amine (free base plus protonated forms). [d] In the presence of 0.005 M borate buffer.