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Reactions of *O*-aryl *S*-aryl dithiocarbonates with pyridines in aqueous ethanol: kinetics and mechanism

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The reactions of *O*-(4-methylphenyl) *S*-(4-nitrophenyl) dithiocarbonate (1), *O*-(4-chlorophenyl) *S*-(4-nitrophenyl) dithiocarbonate (2), and *O*-(4-chlorophenyl) *S*-phenyl) dithiocarbonate (3) with a series of pyridines were subjected to a kinetic investigation in 44 wt% ethanol–water, at 25.0 °C and an ionic strength of 0.2 M. The reactions were followed spectrophotometrically. Under amine excess, pseudo-first-order rate coefficients (k_{obs}) were determined. For the studied reactions, plots of k_{obs} *versus* free pyridine concentration at constant pH were linear, with the slope (k_N) independent of pH. The Brønsted-type plots for (1) and (2) were biphasic, suggesting a stepwise mechanism with a change in the rate-determining step, from breakdown to the formation of a tetrahedral intermediate ($T^{\pm}$), as the basicity of the pyridines increases. For the reactions of (3), at the pK_a range of the pyridines studied, only the breakdown to products of $T^{\pm}$ was observed. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: diaryl dithiocarbonates; kinetics; mechanism; pyridinolysis

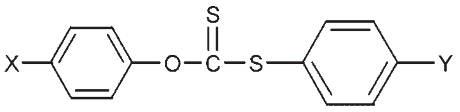
INTRODUCTION

The kinetics and mechanisms of the aminolysis of *O*-alkyl *S*-aryl dithiocarbonates are well documented.[1–10] The reactions of *O*-ethyl *S*-(2,4,6-trinitrophenyl) dithiocarbonate (ETNPDTC) with secondary alicyclic (SA) amines[1,5] and quinuclidines (QUI),[7] and those of *O*-ethyl *S*-(2,4-dinitrophenyl) dithiocarbonate (EDNPDTC) with QUI,[7] in aqueous ethanol at 44 wt%, proceed by a concerted mechanism. Other reactions have been found to be stepwise, through a zwitterionic tetrahedral intermediate. Among these are those of *O*-ethyl *S*-(4-nitrophenyl) dithiocarbonate (ENPDTC) with SA amines, both in water[2] and in aqueous ethanol,[4] as well as those of EDNPDTC with pyridines[8] in water and with SA amines, both in water[1] and aqueous ethanol.[4] Also, the reactions of ETNPDTC with pyridines[8] and SA amines in water[1] are driven by a stepwise mechanism. The reactions of *O*-ethyl *S*-(4-X-phenyl) dithiocarbonates with SA amines (X = H, CH_3O, CH_3, and Cl)[2,3,6] have also been found to be stepwise, through two tetrahedral intermediates, one zwitterionic and the other anionic.

On the other hand, Lee and co-workers have examined the kinetics of the reactions of *O*-ethyl *S*-aryl dithiocarbonates with anilines[9] and benzylamines[10] in acetonitrile, and concluded that these reactions are concerted.

Although the kinetics of the aminolysis of *O*-alkyl *S*-aryl dithiocarbonates has been extensively investigated (see above), that of *O*-aryl *S*-aryl dithiocarbonates has not drawn much attention.[11] We are aware of only a single work on this subject: the aminolysis (SA amines) of *O*-phenyl *S*-(4-nitrophenyl) dithiocarbonate in aqueous ethanol, which shows the presence of two tetrahedral intermediates, one zwitterionic and one anionic.[11]

In order to shed more light on the mechanism of the pyridinolysis of diaryl dithiocarbonates, we report a kinetic study of the reactions of *O*-(4-methylphenyl) *S*-(4-nitrophenyl) dithiocarbonate (**1**), *O*-(4-chlorophenyl) *S*-(4-nitrophenyl) dithiocarbonate (**2**), and *O*-(4-chlorophenyl) *S*-phenyl dithiocarbonate (**3**) with a series of pyridines. By comparing the kinetic results of this work with those of the aminolysis of related compounds, we evaluate the effects of the electrophilic moiety and the non-leaving and leaving groups of the substrate on the kinetics and mechanism.



1 X = Me ; Y = NO_2
2 X = Cl ; Y = NO_2
3 X = Cl ; Y = H

RESULTS AND DISCUSSION

Under amine excess, pseudo-first-order rate constants (k_{obs}) were found for all the reactions. These were obtained by means of the spectrophotometer kinetics software for first-order reactions. The experimental conditions of the reactions and the values of k_{obs} are summarized in Tables 1–3

For the studied reactions, the pseudo-first-order rate constants (k_{obs}), obtained under amine excess, obey Eqn (1), where k_0 and

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Table 1. Experimental conditions and k_{obs} values for the reactions of pyridines with *O*-(4-methylphenyl) *S*-4-nitrophenyl dithiocarbonate (**1**)[a]

Pyridine substituent	pH	F_N[b]	$10^3[N]_{tot}$ (M)[c]	10^3k_{obs} (s^{-1})	Number of runs
4-Oxy	11.2	0.333	3.03–30.3	8.30–98.7	7
	11.5	0.500	1.02–10.2	3.40–38.8	7
	11.8	0.667	2.18–21.8	12.0–114	7
3,4-Diamino	9.15	0.333	3.74–37.4	10.6–59.1	7
	9.45	0.500	10.0–100	25.0–188	7
	9.75	0.667	3.97–39.7	14.9–92.2	7
4-Dimethylamino	8.84	0.333	3.40–34.9	7.50–41.6	7
	9.14	0.500	3.69–36.9	8.90–55.5	7
	8.44	0.667	3.78–37.8	10.4–72.4	7
4-Amino	8.68	0.333	10.3–103	15.1–76.4	7
	8.98	0.500	5.38–53.8	12.7–72.2	7
	9.28	0.667	8.80–88.0	18.6–131	7
3,4-Dimethyl	9.0[d]	0.9995	10.4–104	0.0647–1.04	7
	9.5[d]	0.9998	10.6–106	0.221–0.931	7
	10.0[d]	0.99995	10.3–41.4	0.272–0.440	3
None	9.0[d]	1	12.7–139	0.201–1.61	7
	9.5[d]	1	12.6–126	0.199–1.51	7
	10.0[d]	1	13.4–93.6	0.223–0.930	5

[a] In 44 wt% ethanol–water, at 25.0 °C, and ionic strength 0.2 M (KCl).

[b] Free amine fraction.

[c] Concentration of total amine (free base plus protonated forms).

[d] Under the presence of borate buffer 0.01 M.

Table 2. Experimental conditions and k_{obs} values for the reactions of pyridines with *O*-(4-chlorophenyl) *S*-4-nitrophenyl dithiocarbonate (**2**)[a]

Pyridine substituent	pH	F_N[b]	$10^3[N]_{tot}$ (M)[c]	10^3k_{obs} (s^{-1})	Number of runs
4-Oxy	11.2	0.333	3.03–30.3	18.2–202	7
	11.5	0.500	1.02–10.2	6.50–86.7	7
	11.8	0.667	2.18–21.8	24.0–259	7
3,4-Diamino	9.15	0.333	3.74–37.4	21.6–124	7
	9.45	0.500	10.0–100	56.0–357	7
	9.75	0.667	3.97–39.7	24.0–188	7
4-Dimethylamino	8.84	0.333	3.40–34.9	14.1–90.5	7
	9.14	0.500	3.69–36.9	19.6–124	7
	8.44	0.667	3.78–37.8	23.5–162	7
4-Amino	8.68	0.333	10.3–103	34.6–172	7
	8.98	0.50	5.38–53.8	24.8–155	7
	9.28	0.667	8.80–48.4	38.8–157	4
3,4-Dimethyl	9.0[d]	0.9995	10.5–89.4	0.218–0.964	6
	10.0[d]	0.99995	10.3–104	0.272–1.14	7
None	9.0[d]	1	12.7–108	0.0637–0.144	6
	9.5[d]	1	12.6–126	0.345–1.95	7
	10.0[d]	1	13.4–114	0.599–1.83	6

[a] In 44 wt% ethanol–water, at 25.0 °C, and ionic strength 0.2 M (KCl).

[b] Free amine fraction.

[c] Concentration of total amine (free base plus protonated forms).

[d] Under the presence of borate buffer 0.01 M.

Table 3. Experimental conditions and k_{obs} values for the reactions of pyridines with *O*-(4-chlorophenyl) *S*-phenyl dithiocarbonate (**3**)[a]

Pyridine substituent	pH	F_{N}[b]	$10^3[\mathrm{N}]_{\mathrm{tot}}$ (M)[c]	$10^4 k_{\mathrm{obs}}(\mathrm{s}^{-1})$	Number of runs
4-Oxy	9.0[d]	0.003152	4.77–43.4	2.80–8.14	7
	9.5[d]	0.01	4.63–46.3	5.14–29.0	7
	10.0[d]	0.03065	4.57–45.7	11.4–81.0	7
3,4-Diamino	9.15	0.333	4.72–47.2	0.815–6.36	7
	9.45	0.500	20.7–37.6	4.62–8.53	4
	9.75	0.667	9.76–39.0	1.89–8.00	6
4-Dimethylamino	8.84	0.333	11.0–44.2	3.14–10.4	6
	9.14	0.500	4.32–43.2	2.09–15.8	7
	9.44	0.667	4.14–41.4	2.18–19.0	5
4-Amino	8.68	0.333	7.27–72.7	1.97–7.84	7
	8.98	0.500	18.6–74.3	3.99–14.8	6
	9.28	0.667	6.53–65.3	1.39–16.3	7

[a] In 44 wt% ethanol–water, at 25.0 °C, and ionic strength 0.2 M (KCl).
[b] Free amine fraction.
[c] Concentration of total amine (free base plus protonated forms).
[d] Under the presence of borate buffer 0.01 M.

k_{N} are the rate coefficients for solvolysis and aminolysis of the substrates, respectively, and [N] is the free amine concentration. The values of k_0 and k_{N} showed no dependence on pH within the pH range employed. These values were obtained as the intercept and slope, respectively, of linear plots of k_{obs} against free amine concentration at constant pH

$$k_{\mathrm{obs}} = k_0 + k_{\mathrm{N}}\,[\mathrm{N}] \tag{1}$$

For these reactions, k_0 values were much smaller than the aminolysis term, k_{N} [N], in Eqn (1). The k_{N} values are summarized in Table 4.

The Brønsted-type plots of Fig. 1 were obtained with the data in Table 4. For the pyridinolysis of **1** and **2,** the biphasic Brønsted plots can be explained by the existence of a tetrahedral intermediate ($\mathrm{T}^{\pm}$) and a change in the rate-determining step, from that for k_2 to that for k_1 (see Scheme 1), as the amine becomes more basic.[12–14]

These curves were calculated by means of a semi-empirical equation, Eqn (2), based on the existence of a zwitterionic tetrahedral intermediate ($\mathrm{T}^{\pm}$) on the reaction pathway (see Scheme 1).[12] A similar equation has been reported by Gresser and Jencks.[13]

Equation 2 contains four parameters: β_1 and β_2, which are the Brønsted slopes at high and low pK_{a}, respectively, and k_{N}^0 and pK_{a}^0, which are the corresponding values at the center of the Brønsted curvature.

$$\log\left(\frac{k_{\mathrm{N}}}{k_{\mathrm{N}}^0}\right) = \beta_2(\mathrm{p}K_{\mathrm{a}} - \mathrm{p}K_{\mathrm{a}}^0) - \log\left(\frac{1+a}{2}\right) \tag{2}$$

$$\log a = (\beta_2 - \beta_1)(\mathrm{p}K_{\mathrm{a}} - \mathrm{p}K_{\mathrm{a}}^0)$$

The Brønsted curves were calculated by means of the following parameters: log $k_{\mathrm{N}}^0 = 0.33$, p$K_{\mathrm{a}}^0 = 9.0$, $\beta_1 = 0.12$ and $\beta_2 = 0.83$ ($n = 6$, $R^2 = 0.99991$) for the reactions of **1** and log $k_{\mathrm{N}}^0 = 0.71$, p$K_{\mathrm{a}}^0 = 9.1$, $\beta_1 = 0.11$ and $\beta_2 = 0.89$ ($n = 6$, $R^2 = 0.9995$) for the reactions of **2**. The errors of the slopes are ±0.1, and those of pK_{a}^0 and log k_{N}^0 are ±0.2 and ±0.1, respectively. These values of β_1 and β_2 are in accordance with those reported for other aminolyses governed by stepwise mechanisms: $\beta_1 = 0.1$–0.3 and $\beta_2 = 0.8$–1.1[1,2,4,7,8,12–14]

Table 4. Values of pK_{a} for the conjugate acids of pyridines and k_{N} values for the reactions of pyridines with *O*-(4-methylphenyl) *S*-(4-nitrophenyl) dithiocarbonate (**1**), *O*-(4-chlorophenyl) *S*-(4-nitrophenyl) dithiocarbonate (**2**) and *O*-(4-chlorophenyl) *S*-phenyl dithiocarbonate (**3**)[a]

Pyridine substituent	pK_{a}	k_{N} ($\mathrm{s}^{-1}\,\mathrm{M}^{-1}$)		
		1	**2**	**3**
4-Oxy	11.5	8.8 ± 0.4	19.3 ± 0.8	5.6 ± 0.1
3,4-Diamino	9.45	3.4 ± 0.1	6.6 ± 0.2	0.032 ± 0.002
4-Dimethylamino	9.14	2.8 ± 0.1	6.1 ± 0.2	0.068 ± 0.002
4-Amino	8.98	2.1 ± 0.1	4.7 ± 0.2	0.037 ± 0.001
3,4-Dimethyl	5.68	0.0083 ± 0.0001	0.0088 ± 0.0005	
None	4.63	0.0011 ± 0.00005	0.0012 ± 0.00007	

[a] Both the pK_{a} and k_{N} values were determined in 44 wt% ethanol–water, at 25.0 °C, and ionic strength 0.2 M (KCl).

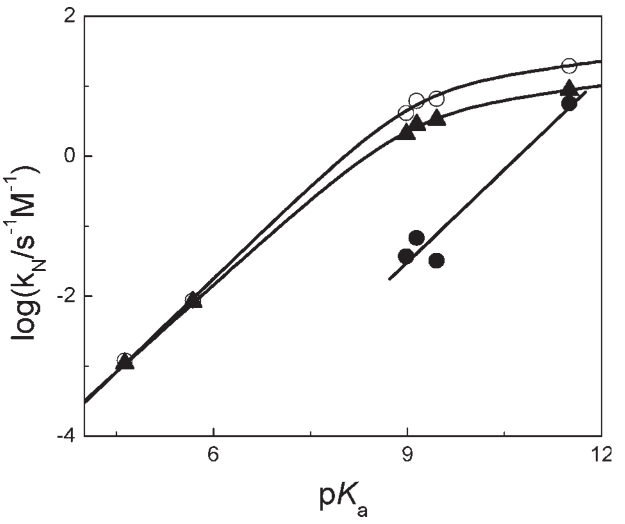


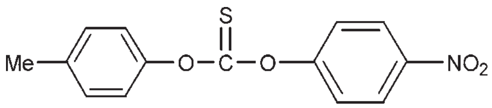
Figure 1. Brønsted plots obtained for the pyridinolysis of dithiocarbonates **1** (▲), **2** (○), and **3** (●) in 44 wt% ethanol–water, at 25.0 °C, ionic strength 0.2 M (KCl)

For the pyridinolysis of dithiocarbonate **3,** a linear Brønsted plot with a slope of 0.88 was obtained (see Fig. 1), which indicates that for these reactions decomposition to products of the intermediate, $T^{\pm}$ is the rate-limiting step.[12–14]

Effect of the leaving group

The pyridinolysis of **2** shows a biphasic Brønsted plot with the curvature center (pK_a^0) at a pK_a of 9.1. Nevertheless, for the reactions of the same amines with **3,** the linear Brønsted plot with high slope shows that the k_2 step is rate-determining for the whole pK_a range. This means that for the reactions of this substrate, the pK_a^0 value is greater than 11.5. The lower pK_a^0 value for the pyridinolysis of **2** is reasonable, in view of the greater nucleofugality (greater k_2 value) of 4-nitrobenzenethiolate in **2** compared with benzenethiolate in **3**. It is known that a greater k_2/k_{-1} ratio shifts the center of the Brønsted curvature towards lower values (see below).[12–14]

In the same line, the reaction of 4-methylphenyl 4-nitrophenyl thionocarbonate (**4**) with pyridines, at the same experimental conditions as those of this study, is governed by a stepwise mechanism, being the expulsion of the nucleofuge, the rate-determining step for the whole pK_a range.[15] This suggests that the pK_a^0 must be greater than 9.1.[15] Nevertheless, pyridinolysis of **1** (this study) shows a biphasic Brønsted plot with the curvature center at p$K_a^0 = 9.0$. This result indicates a greater leaving ability (greater k_2 in Scheme 1) of 4-nitrobenzenethiolate, relative to 4-nitrophenoxide, from the corresponding intermediates $T^{\pm}$ (see below). Although phenoxides are better nucleofuges than *isobasic* benzenethiolates,[16] the above result can be explained by the rather large difference in basicity of the groups involved (p$K_a = 4.5$ and 7.5 in aqueous ethanol for 4-nitrobenzenethiol and 4-nitrophenol, respectively).



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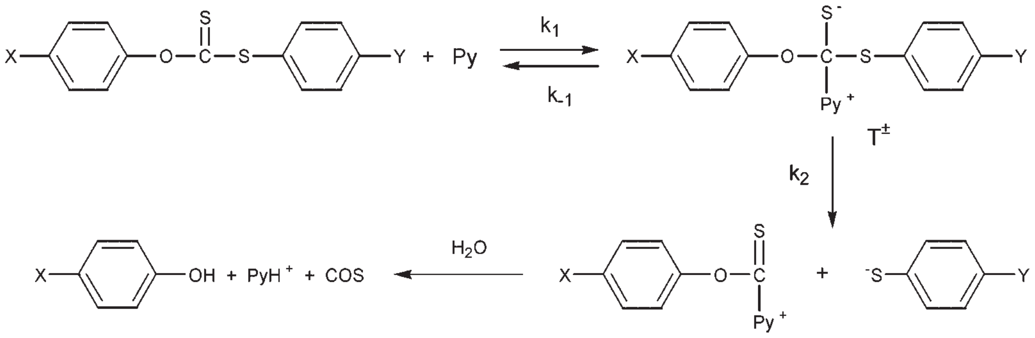
On the other hand, the pyridinolysis of aryl chlorothionoformates[17] is stepwise with the formation of the intermediate $T^{\pm}$as the rate-determining step for the whole pK_a range of the pyridines studied, showing that chloride is a better nucleofuge than 4-nitrobenzenethiolate from the corresponding tetrahedral intermediate.

Effect of the non-leaving group

It can be observed from Table 4 and Fig. 1 that the k_N values for the reactions with pyridines of p$K_a > 9.0$ are greater for **2** than for **1**. For the reactions of both substrates with 4-oxypyridine (an amine with pK_a greater than pK_a^0 for the reactions of both substrates), the first step is rate-determining, and $k_N = k_1$. Therefore, Table 4 shows that the k_1 value for **2** is twice as great as that for **1**. This result can be explained by the greater electron-withdrawing effect of Cl than CH_3 (σ_P values are 0.23 and −0.17, respectively),[18] which leads to a more positive thiocarbonyl group for **2** and, therefore, leaves it more prone to nucleophilic attack by the amine.

On the other hand, for amines with p$K_a <$ pK_a^0 the rate-determining step is expulsion of the leaving group from the $T^{\pm}$ intermediate (k_2 in Scheme 1); for these amines, $k_N = k_1k_2/k_{-1}$. It can be observed from Fig. 1 that for pyridines with pK_a lower than pK_a^0, the k_N values for the reactions of **1** and **2** are closely similar. Since the k_1 values are larger for the pyridinolysis of **2**, necessarily the k_2/k_{-1} values must be larger for the pyridinolysis of **1**; this is in accordance with an equation derived from the hypothesis of the tetrahedral intermediate (Eqn 3),[8,19] which predicts a larger k_2 value for a smaller pK_a^0.

$$\log\left(\frac{k_{-1}}{k_2}\right) = (\beta_2 - \beta_1)(\mathrm{p}K_a^0 - \mathrm{p}K_a) \qquad (3)$$

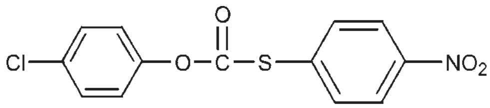


Scheme 1.

Effect of the electrophilic group

The pyridinolysis of dithiocarbonate **2** (this study) and that of 4-clorophenyl *S*-(4-nitrophenyl) thiolcarbonate (**5**),[20] under the same experimental conditions, are driven by a stepwise mechanism, as judged by the biphasic Brønsted plots found with pK_a^0 9.1 and 7.9, respectively. It is known that the change of thiocarbonyl by carbonyl as the electrophilic group, enlarges both k_{-1} and k_2, due to the greater energy of the π bond of CO as compared with that of CS (by 40 kcal/mol), which enhances the driving force of O$^-$ (relative to S$^-$) in the intermediate to form a double bond and expel both the amine and the leaving group of the substrates.[14,21] The fact that the pK_a^0 value for the pyridinolysis of thiolcarbonate **5** (7.9) is smaller than that for **2** (9.1) indicates that k_2 increases more than k_{-1} by the change of CS in the latter substrate by CO in the former (see Eqn 3).

The reaction of 4-oxypyridine with thiolcarbonate **5** is about 15 times faster than that with **2** (for both reactions $k_N = k_1$),[20] which means that pyridine attack to the CO group is faster than that to CS, when formation of the intermediate T$^\pm$ is rate-limiting. This is in accordance with the larger k_1 values found for the pyridinolysis of *S*-(2,4-dinitrophenyl) and *S*-(2,4,6-trinitrophenyl) ethyl thiolcarbonates (**6** and **7**, respectively)[22] , compared with those for the same aminolysis of the corresponding dithiocarbonates.[8]



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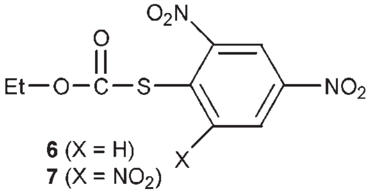

6 (X = H)
7 (X = NO$_2$)

CONCLUDING REMARKS

From the results obtained in this work, several conclusions can be drawn: (i) The mechanism of the pyridinolysis of **1**–**3** is stepwise. The k_1 value for **2** is twice of that for **1**, in line with the greater electron-withdrawing ability of 4-chloro than 4-methyl in the non-leaving group. (ii) The pyridinolysis of **2** shows a smaller pK_a^0 value than that for the same aminolysis of the corresponding thionocarbonate due to the faster nucleofugality from the intermediate T$^\pm$ of 4-nitrobenzenethiolate relative to 4-nitrophenoxide. (iii) The pyridinolyses of **2** and the corresponding thiolcarbonate are stepwise with pK_a^0 values of 9.1 and 7.9, respectively, showing that the k_{-1}/k_2 ratio is larger for the former reactions. (iv) For the pyridinolysis of **3,** the rate-limiting step is the decomposition of T$^\pm$ to products.

EXPERIMENTAL

Materials

The substrates **1** and **2** were synthesized by the reaction of the corresponding aryl chlorothionoformate with 4-nitrobenzenethiolate, as previously described for the preparation of *O*-phenyl *S*-(2,4-dinitrophenyl) dithiocarbonate.[11] Compound **3** was synthesized by the reaction of phenyl chlorodithioformate with 4-chlorophenoxide, as reported.[23] The solid products showed the following characteristics.

1: m.p. 93–94 °C. ^{1}HNMR (400 MHz, CDCl$_3$) δ PPM: 2.36 (s, 3H); 6.96 (d, 2H J = 8.4 Hz); 7.21 (d, 2H, J = 8.4 Hz); 7.80 (d, 2H J = 8.8 Hz); 8.30 (d ,2H J = 8.8 Hz). ^{13}CNMR (200 MHz,CDCl$_3$) δ ppm: 21.18, 121.58, 124.52, 130.45, 136.06, 137.03, 138.24, 148.95, 152.31, 210.28.

2: m.p. 107–108 °C (lit[23] 109–111 °C). ^{1}HNMR (400 MHz, CDCl$_3$) δ PPM: 7.03 (d, 2H, J = 8.4 Hz); 7.38(d, 2H, J = 8.4 Hz); 7.79(d, 2H, J = 8.4 Hz); 8.31 (d, 2H, J = 8.4 Hz); ^{13}CNMR (200 MHz, CDCl$_3$) δ PPM: 123.64, 124.60, 130.03, 132.76, 136.17, 137.85, 149.06, 152.70, 210.02.

3: m.p. 68–69 °C (lit[23] 68–69 °C). ^{1}HNMR (400 MHz, CDCl$_3$) δ PPM: 7.02 (d, 2H J = 8.8 Hz); 7.7.46(d, 2H J = 8.8 Hz); 7.47 (m, 3H); 7.61(m, 2H); ^{13}CNMR (200 MHz, CDCl$_3$): 123.65, 129.77, 129.86,130.32,130.69, 132.38, 135.39, 153.01, 213.23.

Kinetic measurements

The kinetics of the reactions was analyzed through a diode array spectrophotometer in 44 wt% ethanol–water, at 25.0 ± 0.1 °C and an ionic strength of 0.2 M (maintained with KCl). The reactions were followed at 420 nm (appearance of 4-nitrobenzenethiolate anion) for the reactions of **1** and **2,** and at 325–350 nm (appearance of the corresponding 1-(4-chlorophenoxy)thiocarbonylpyridinium cation) for the reactions of **3**.

The reactions were studied under at least 10-fold amine excess over the substrate, the initial concentration of the latter being 2.5×10^{-5} M. Under these conditions, pseudo-first-order rate coefficients (k_{obs}) were found throughout, and the reactions were followed for at least five half-lives. For all the reactions, the pH was maintained constant (three pH values for each amine), either by the buffer formed by partial protonation of the amine or by the addition of an external buffer.

The experimental conditions of the reactions are shown in Tables 1–3.

Product studies

4-Nitrobenzenethiolate anion was identified as one of the products of the reactions of **1** and **2**. This was carried out by comparison of the UV–Vis spectra after completion of these reactions with that of an authentic sample of 4-nitrobenzenethiol, under the same experimental conditions.

For the reactions of **3,** an increase and decrease of absorbance at 325–350 nm was observed, attributed to the formation and hydrolysis of the corresponding pyridiniumcarbamate cation, by analogy with the pyridinolysis of aryl chlorothionoformates.[17]

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