

Phenolysis of diaryl thiocarbonates and thionocarbonates

Enrique A. Castro^{a*}, Marjorie Cepeda^a, Paulina Pavez^a
and José G. Santos^{a*}

The phenolysis of phenyl 5-4-nitrophenyl thiocarbonate (1), 4-chlorophenyl 5-4-nitrophenyl thiocarbonate (2), phenyl 4-nitrophenyl thionocarbonate (3), 3-chlorophenyl 4-nitrophenyl thionocarbonate (4) and 3-methoxyphenyl 4-nitrophenyl thionocarbonate (5) are studied kinetically in 44 wt% ethanol–water, at 25.0 °C, ionic strength 0.2 M. The Brønsted plots ($\log k_N$ vs. pK_a of phenols) for the reactions of 1 and 2 are linear and those of 3, 4 and 5 are curved. The Brønsted slopes for 1 and 2 are 0.64 and 0.60, respectively, which suggest a concerted mechanism for these reactions. The curved Brønsted plots for the reactions of 3, 4 and 5 show slope values of 1.0, 1.1 and 1.1, respectively, at low pK_a , and 0.39, 0.28 and 0.34, respectively, at high pK_a . The shape and slope values of these Brønsted plots are in accordance with a stepwise mechanism. The reactivity towards phenoxides of the thiocarbonates increases with the increase in the Hammett σ value for the substituents in the non-leaving group. The fact that the phenolysis of 3 is stepwise, whereas that of phenyl 4-nitrophenyl carbonate is concerted can be attributed to the destabilization of the intermediate T^- . A similar argument explains the stepwise phenolysis of 3, in contrast to the concerted phenolysis of 1, where there is an additional destabilization of T^- caused by the change of the leaving group, from 4-nitrophenoxide in 3 to 4-nitrobenzenethiolate in 1. Thiocarbonates 1 and 2 in 44 wt% ethanol–water are less reactive towards phenoxide anions (ca. 100-fold) than their corresponding oxycarbonates in water. Copyright © 2008 John Wiley & Sons, Ltd.

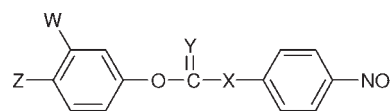
Keywords: phenolysis; thiocarbonates; kinetics; mechanism; Brønsted plots

INTRODUCTION

There have been many reports on the kinetics and mechanisms of the phenolysis of esters^[1–6] and thioesters,^[7,8] but less regarding the phenolysis of methyl aryl carbonates,^[9] diaryl carbonates,^[10–12] *O*-alkyl *S*-aryl thiocarbonates^[8,13] alkyl aryl thionocarbonates^[8,11,14] and diaryl thionocarbonates.^[8,11,14]

The kinetic studies on the phenolysis of methyl aryl carbonates^[9] and *O*-ethyl *S*-aryl thiocarbonates^[13] show concerted mechanisms, in contrast to those of methyl aryl thionocarbonates, which show stepwise mechanisms.^[11,14] To our knowledge, there are only two works in the literature on the mechanism of the phenolysis of diaryl thionocarbonates (that of bis(4-nitrophenyl) thionocarbonate^[11] and phenyl 2,4-dinitrophenyl thionocarbonate^[14]) and there are no reports on the phenolysis of *O*-aryl *S*-aryl thiocarbonates.

In this work, we examine the kinetics and mechanisms of the phenolysis of phenyl 5-4-nitrophenyl thiocarbonate (1), 4-chlorophenyl 5-4-nitrophenyl thiocarbonate (2), phenyl 4-nitrophenyl thionocarbonate (3), 3-chlorophenyl 4-nitrophenyl thionocarbonate (4) and 3-methoxyphenyl 4-nitrophenyl thionocarbonate (5). The aim is to shed more light on the mechanism of the phenolysis of thiocarbonates, specifically the diaryl derivatives, and to study the effect of the leaving, non-leaving and electrophilic groups of these compounds on the kinetics and mechanisms of these reactions.



- 1 (X = S, Y = O, Z = W = H)
2 (X = S, Y = O, Z = Cl, W = H)
3 (X = O, Y = S, Z = W = H)
4 (X = O, Y = S, Z = H, W = Cl)
5 (X = O, Y = S, Z = H, W = OMe)

RESULTS AND DISCUSSION

For all reactions, pseudo-first-order rate coefficients (k_{obs}) were obtained (under total phenol excess). The experimental

* Correspondence to: E. A. Castro or J. G. Santos, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 6094411, Chile. E-mail: jgsantos@uc.cl

a E. A. Castro, M. Cepeda, P. Pavez, J. G. Santos
Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 6094411, Chile

conditions of the reactions and the values of k_{obs} are shown in Tables 1–5, in Supplementary Materials.

The rate law obtained for all the reactions studied is given by Eqns (1) and (2), where P, S and ArO^- represent the product (either 4-nitrophenoxide or 4-nitrobenzenethiolate anions), the substrate and a substituted phenoxide nucleophile, respectively; k_0 is the rate coefficient for solvolysis and k_{N} is the rate coefficient for phenolysis of the substrate. The value of k_0 was much lower than that of $k_{\text{N}} [\text{ArO}^-]$ in Eqn (2).

$$\frac{d[\text{P}]}{dt} = k_{\text{obs}} [\text{S}] \quad (1)$$

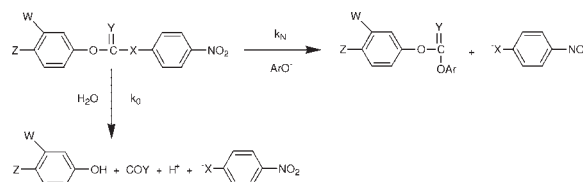
$$k_{\text{obs}} = k_0 + k_{\text{N}} [\text{ArO}^-] \quad (2)$$

The values of k_{N} for all reactions were obtained as the slopes of the linear plots of k_{obs} versus $[\text{ArO}^-]$ and were found to be pH independent. These k_{N} values are shown in Table 1, together with the $\text{p}K_{\text{a}}$ values of the series of nucleophiles employed. The overall reactions studied in this work are shown in Scheme 1, where W, X, Y and Z were defined in Introduction.

Figures 1 and 2 show the Brønsted-type plots obtained with the values of k_{N} and $\text{p}K_{\text{a}}$ in Table 1 (measured under the same experimental conditions). The Brønsted plots for the phenolysis of thiolcarbonates **1** and **2** are linear (Fig. 1), with slopes (β) 0.64 and 0.60, respectively, whereas those for thionocarbonates **3**, **4** and **5** are curved (Fig. 2).

I.-Phenolysis of thiolcarbonates **1** and **2**

The values of the Brønsted slopes found for the reactions of both thiolcarbonates **1** and **2** are in accordance with those obtained in the concerted phenolysis of the following carbonates: 4-nitrophenyl, 2,4-dinitrophenyl and 2,4,6-trinitrophenyl methyl carbonates ($\beta = 0.67$, 0.48 and 0.52, respectively),^[9] phenyl, 4-nitrophenyl, 4-chlorophenyl and 4-methylphenyl 4-nitrophenyl carbonates ($\beta = 0.61$, 0.66, 0.67 and 0.48, respectively)^[10–12] and phenyl, 4-chlorophenyl and 4-methylphenyl 2,4-dinitrophenyl carbonates ($\beta = 0.49$, 0.32 and 0.41, respectively).^[10,12] The slopes of the plots in Fig. 1 are also in agreement with the concerted phenolysis of the following esters: 4-chloro-2-nitrophenyl acetate ($\beta = 0.64$),^[2] 2,4-dinitrophenyl acetate ($\beta = 0.59$),^[3] 3-nitrophenyl, 4-nitrophenyl and 3,4-dinitrophenyl formates ($\beta = 0.64$, 0.51 and 0.43, respectively)^[15] and the corresponding acetates ($\beta = 0.66$, 0.59 and 0.53, respectively).^[15] They are also in line with the



Scheme 1.

slopes found in the concerted phenolysis of phthalic and maleic anhydrides ($\beta = 0.45$ and 0.56, respectively).^[16] Therefore, the β values obtained in the phenolysis of the thiolcarbonates studied in this work suggest that these reactions are ruled by a concerted mechanism.

Nevertheless, the magnitude of β is not sufficient to validate the concerted mechanism.^[17,18] For the reactions of **1** and **2**, where 4-nitrobenzenethiolate anion is the leaving group, it is difficult to predict the position of the centre of the curvature if the mechanism were stepwise, due to the fact that nucleophile (phenoxide anions) and nucleofuge (4-nitrobenzenethiolate) are of different nature. Nonetheless, we are inclined towards a concerted mechanism based on the following grounds: (i) The phenolysis of ethyl *S*-aryl thiolcarbonates^[13] and the benzenethiolysis of methyl aryl carbonates^[19] were found to be concerted, showing that the presence of one alkyl (methyl or ethyl), one phenoxy and one benzenethio groups in an anionic tetrahedral intermediate destabilizes the putative tetrahedral intermediate. (ii) The phenolysis reactions of a series of diaryl carbonates are concerted, showing that the presence of three phenoxy groups destabilizes the putative tetrahedral intermediate.^[10–12] Therefore, an anionic tetrahedral intermediate with two phenoxy and one benzenethio groups should be very unstable, enforcing a concerted mechanism. Scheme 2 shows the probable mechanism for the phenolysis of thiolcarbonates **1** and **2**.

Effect of the non-leaving group

It can be observed in Table 1 that the nucleophilic rate constants for the phenolysis of 4-chlorophenyl *S*-4-nitrophenyl thiolcarbonate (**2**) are greater than those for the same reactions of phenyl *S*-4-nitrophenyl thiolcarbonate (**1**). This result is in accordance with the greater electron-withdrawing ability of 4-chlorophenoxy compared to phenoxy,^[20] which leaves the carbonyl carbon atom of the former substrate more positive and, in consequence, more prone to nucleophilic attack.

Table 1. Values of $\text{p}K_{\text{a}}$ for the conjugate acids of phenols and k_{N} values for the reactions of phenoxides with phenyl *S*-4-nitrophenyl thiolcarbonate (**1**), 4-chlorophenyl *S*-4-nitrophenyl thiolcarbonate (**2**), phenyl 4-nitrophenyl thionocarbonate (**3**), 3-chlorophenyl 4-nitrophenyl thionocarbonate (**4**) and 3-methoxyphenyl 4-methoxyphenyl thionocarbonate (**5**)^a

Phenoxide substituent	$\text{p}K_{\text{a}}$	$10^2 k_{\text{N}}/\text{s}^{-1} \text{mol}^{-1} \text{dm}^3$				
		1	2	3	4	5
4-OCH ₃	11.55	260 ± 10	458 ± 15			
H	11.16	37 ± 1	151 ± 5	32.2 ± 0.6	68.9 ± 0.9	53 ± 2
4-Cl	10.47		58 ± 3	25.1 ± 0.4	81 ± 2	43 ± 1
3-Cl	10.23	23.0 ± 0.7	72 ± 2			
4-CN	8.60	2.6 ± 0.1	7.1 ± 0.3	5.1 ± 0.1	16.7 ± 0.4	9.7 ± 0.3
2,6-F ₂	7.82		2.1 ± 0.1	0.79 ± 0.03	6.2 ± 0.2	2.3 ± 0.1
2,3,4,5,6-F ₅	5.45	0.017 ± 0.001		0.0086 ± 0.0001	0.056 ± 0.005	0.024 ± 0.002

^a Both the $\text{p}K_{\text{a}}$ and k_{N} values were determined in 44 wt% ethanol–water, at 25.0 °C, ionic strength 0.2 mol dm⁻³ (KCl).

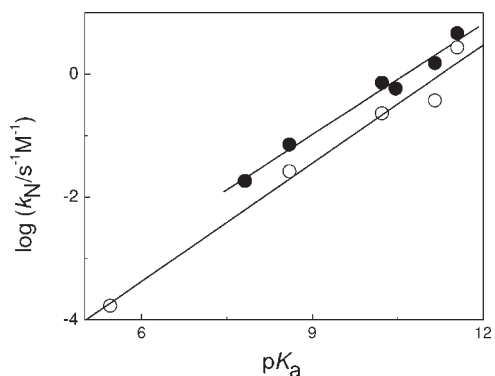


Figure 1. Brønsted-type plots obtained for the phenolysis of **1** (o) and **2** (●) in 44 wt% ethanol–water, 25.0 ± 0.1 °C, ionic strength 0.2 mol dm^{-3} (KCl)

On the other hand, the change of the ethyl group in ethyl *S*-(4-nitrophenyl) thiolcarbonate^[13] for an aryl group (phenyl and 4-chlorophenyl in **1** and **2**, respectively, this study) does not change the mechanism of the phenolysis (all concerted), although increases the nucleophilic rate constant by more than 10-fold. Since the former reaction was measured in water (which should increase the k_N value compared with aqueous ethanol) and the two latter in 44% aqueous ethanol, the increase of k_N can be attributed to the greater electron withdrawal of the aryl groups in **1** and **2** relative to the ethyl group in the former thiolcarbonate.^[20]

Effect of the leaving group

The phenolysis reactions of phenyl 4-nitrophenyl and 4-chlorophenyl 4-nitrophenyl carbonates in water are driven by concerted mechanisms.^[10,12] Similarly, the phenolyses of **1** and **2** in 44 wt% ethanol–water are also ruled by a concerted mechanism (this work). This is reasonable since the substitution of *O*-4-nitrophenyl by *S*-4-nitrophenyl as the leaving group of the substrates should further destabilize the hypothetical anionic tetrahedral intermediate (T^-), due to the greater nucleofugality of the latter group. Moreover, the change of solvent from water to aqueous ethanol should also destabilize the putative intermediate T^- in view of the lower polarity of the latter solvent mixture.

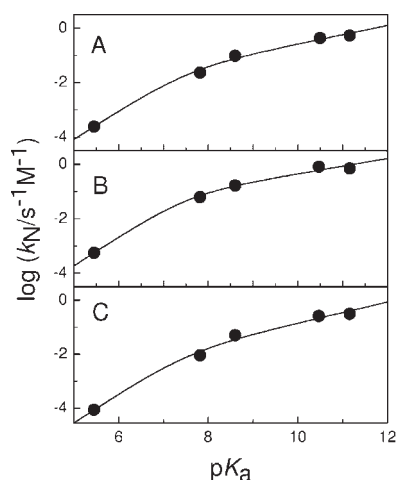
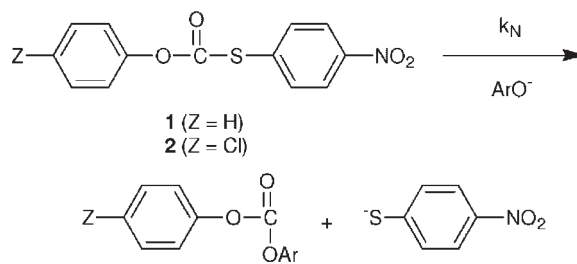


Figure 2. Brønsted-type plots obtained for the phenolysis of **3** (C), **4** (B) and **5** (A) in 44 wt% ethanol–water, 25.0 ± 0.1 °C, ionic strength 0.2 mol dm^{-3} (KCl)



Scheme 2.

A comparison of the nucleophilic rate constants (k_N) for the phenolysis of thiolcarbonates **1** and **2** in 44 wt% ethanol–water (this work) with those of the same reactions of phenyl and 4-chlorophenyl 4-nitrophenyl carbonates in water^[10,12] shows that the carbonates are more reactive (about 80–100-fold) than the corresponding thiolcarbonates towards a given phenoxide. This is in accordance with the larger k_N values found in the following reactions when a benzenethiolate leaving group is substituted by its phenoxide analogue: (i) the phenolysis of alkyl aryl carbonates^[9] compared with that of alkyl aryl thiolcarbonates^[13] (10–40-fold); (ii) the phenolysis of methyl 2,4-dinitrophenyl thionocarbonate,^[14] relative to that of *O*-ethyl 2,4-dinitrophenyl dithiocarbonate;^[14] (iii) the benzenethiolysis of methyl aryl carbonates^[19] compared with that of ethyl *S*-aryl thiolcarbonates^[19] (2–5-fold). Also, the reactions of secondary alicyclic amines with methyl 2,4,6-trinitrophenyl carbonate^[21] show greater k_N values than those with ethyl *S*-(2,4,6-trinitrophenyl) thiolcarbonate.^[22]

All the above cases have been explained by the greater steric hindrance of the sulphur atom than oxygen in the leaving group, which makes nucleophilic attack to the former substrate more difficult. This effect is also present when the *S* atom is in the non-leaving group: the reactions of secondary alicyclic amines,^[23] quinuclidines^[23] and phenols^[9] with methyl 2,4-dinitrophenyl carbonate are faster than the corresponding reactions with *S*-methyl 2,4-dinitrophenyl thiolcarbonate.^[24,25]

Therefore, the smaller k_N values found for the phenolysis of **1** and **2** in aqueous ethanol, in comparison with those for the same reactions of analogous diaryl carbonates in water can be attributed in part to a greater steric hindrance to nucleophilic attack by the thiolcarbonates. On the other hand, the change of solvent from water to aqueous ethanol should also be in part responsible for the slower reactions of thiolcarbonates in aqueous ethanol, relative to those of carbonates in water.

II. Phenolysis of thionocarbonates 3–5

These reactions show the curved Brønsted plots in Fig. 2. The curves in this figure were calculated by a semiempirical equation (Eqn (3)) derived from the existence of a tetrahedral intermediate on the reaction pathway and a change in the rate-determining step.^[26] In this equation, β_1 and β_2 are the slopes at high and low pK_a , respectively, and $\log k_N^0$ and pK_a^0 are the corresponding parameters at the centre of the Brønsted curvature:

$$\log(k_N/k_N^0) = \beta_2(pK_a - pK_a^0) - \log((1 + \alpha)/2) \quad (3)$$

$$\log \alpha = (\beta_2 - \beta_1)(pK_a - pK_a^0)$$

Taking into account that for all these reactions the leaving group is 4-nitrophenoxide anion and the condition for pK_a^0

($k_2 = k_{-1}$) is satisfied when the pK_a for the phenoxide nucleophile is equal to that for the nucleofuge, for the fittings we used a pK_a^0 value of 7.5 (the pK_a of 4-nitrophenol) as a fixed parameter and adjust the other parameters in Eqn (3) by a nonlinear least-squares fitting.

The fitting parameters obtained for the Brønsted curves are: $\beta_1 = 0.39$, $\beta_2 = 1.00$, $pK_a^0 = 7.5$ and $\log k_N^0 = -2.12$ for thionocarbonate **3**; $\beta_1 = 0.28$, $\beta_2 = 1.07$, $pK_a^0 = 7.5$ and $\log k_N^0 = -1.35$ for thionocarbonate **4** and $\beta_1 = 0.34$, $\beta_2 = 1.06$, $pK_a^0 = 7.5$ and $\log k_N^0 = -1.73$ for thionocarbonate **5**.

The fit of the calculated curves to the experimental points in Fig. 2 suggests that these reactions proceed through an anionic tetrahedral intermediate (T^-) and there is a change of the rate-determining step, from formation of T^- to its breakdown as the pK_a of the phenol decreases (refer Scheme 3).

The β_1 and β_2 values found are in agreement with those obtained in the stepwise phenolyses of methyl 4-nitrophenyl and bis(4-nitrophenyl) thionocarbonates.^[11] The β_1 values are also in accordance with those found in the stepwise phenolyses of methyl and phenyl 2,4-dinitrophenyl thionocarbonates.^[14]

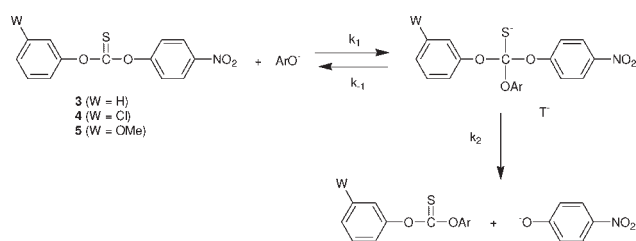
Effect of the non-leaving group

Figure 2 shows that for the reactions of thionocarbonates **3–5** with the two most basic phenoxide anions (pK_a of the corresponding phenols greater than 7.5), the formation of the anionic tetrahedral intermediate (T^-) is the rate-determining step. Therefore, for the reactions of these nucleophiles, $k_N = k_1$. Table 1 shows that for the reactions of these two most basic phenoxide ions, the k_1 value increases in the sequence **3** < **5** < **4**. This is the same sequence as that for σ_m for the substituents in the non-leaving group of the substrates: $H < 3-OCH_3 < 3-Cl$.^[20] A Hammett plot ($\log k_1$ vs. σ_m , not shown) for the reactions of thionocarbonates **3–5** with three different phenoxides shows a reaction constant, ρ ca. 1.3. The positive value of this parameter is in accordance with the fact that the greater the electron-withdrawing effect from the non-leaving group the greater should be k_1 because the carbonyl carbon gets more positive and, therefore, more prone to nucleophilic attack.

From the hypothesis of the tetrahedral intermediate Eqn (4) can be deduced:^[27]

$$\log(k_{-1}/k_2) = (\beta_2 - \beta_1)(pK_a^0 - pK_a) \quad (4)$$

Taking into account that for the three thionocarbonates the pK_a^0 value is the same and that the values of β_1 and β_2 for the three substrates are closely similar (as shown above), Eqn (4) shows that the ratio k_{-1}/k_2 is similar for the three substrates (in their reaction with the same phenoxide ion). For phenoxide anions less basic than 4-nitrophenoxide (of corresponding pK_a less than 7.5), $k_N = k_1 k_2 / k_{-1}$ and therefore the sequence of k_N values for the reactions of these phenoxide ions with the three



Scheme 3.

thionocarbonates should be the same as that for k_1 . Unfortunately, the series of phenoxides employed in this work contains only one nucleophile less basic than 4-nitrophenoxide: pentafluorophenoxide. Table 1 shows that for this nucleophile the sequence of reactivity (**3** > **5** > **4**) is the same as that for the most basic nucleophiles (for which $k_N = k_1$).

Effect of the electrophilic group (CS vs. CO)

The fact that the phenolysis of **3** in aqueous ethanol is stepwise (this study) is in contrast to the finding that the same reaction of phenyl 4-nitrophenyl carbonate in water is concerted.^[10] The latter mechanism was deduced from the linear Brønsted plot, with slope 0.61, obtained.^[10] The change of solvent, from aqueous ethanol to water, should not be responsible for this change in mechanism, since water should stabilize the anionic tetrahedral intermediate (T^-) compared to aqueous ethanol. These results indicate that the change of thiocarbonyl by carbonyl as the electrophilic group destabilizes the intermediate T^- in such a way that the mechanism changes from stepwise to concerted. This is the same effect as that found for the phenolysis of 4-nitrophenyl and 2,4-dinitrophenyl methyl thionocarbonates (stepwise mechanisms)^[11,14] and the corresponding carbonates (concerted processes).^[9] Other examples are: (i) the phenolysis of bis(nitrophenyl) thionocarbonate is stepwise,^[11] whereas that of bis(nitrophenyl) carbonate is concerted^[11] and (ii) the phenolysis of phenyl 2,4-dinitrophenyl thionocarbonate is driven by a stepwise mechanism,^[14] in contrast to that of phenyl 2,4-dinitrophenyl carbonate, which is concerted.^[10]

The above results have been explained in terms of a destabilization of the tetrahedral intermediate due to the greater ability of O^- than S^- in the intermediate to form the double bond with the central carbon and expel both the leaving group and the nucleophile. This is due to the stronger π -bonding energy of the $C=O$ group (by 40 kcal) relative to $C=S$.^[28]

CONCLUSIONS

The reactions of the thionocarbonates **1–5** with a series of phenols are studied kinetically in 44 wt% ethanol–water. The Brønsted slopes, together with other evidence, suggest a concerted mechanism for the phenolysis of phenyl 5-(4-nitrophenyl) thionocarbonate (**1**) and 4-chlorophenyl 5-(4-nitrophenyl) thionocarbonate (**2**) and a stepwise process for the phenolysis of phenyl 4-nitrophenyl thionocarbonate (**3**), 3-chlorophenyl 4-nitrophenyl thionocarbonate (**4**) and 3-methoxyphenyl 4-nitrophenyl thionocarbonate (**5**).

Comparing the kinetics and mechanisms of these reactions with those of similar reactions, the following conclusions arise:

- The phenolysis of thiolcarbonate **2** is faster than that of thiolcarbonate **1**, in accordance with the greater electron withdrawal of 4-chlorophenoxy than phenoxy as non-leaving group.
- The change of the ethyl group in ethyl 5-(4-nitrophenyl) thiolcarbonate by an aryl group (4-chlorophenyl and phenyl in **1** and **2**, respectively) increases the reactivity towards phenoxides more than 10-fold.
- The smaller k_N values found in the phenolysis of thiolcarbonates **1** and **2** in 44 wt% ethanol–water in comparison with those for the same reactions of analogous diaryl carbonates in water (80–100-fold) are attributed in part to a greater steric

hindrance to phenoxide attack by 4-nitrobenzenethio compared with 4-nitrophenoxy. The change of solvent also plays a part.

- (iv) The k_1 values for the phenolysis of thionocarbonates **3–5** increase in the sequence $\mathbf{3} < \mathbf{5} < \mathbf{4}$, which is the same sequence as that for σ_m for the substituents in the non-leaving group of substrates.
- (v) The phenolysis of thionocarbonate **3** is stepwise, in contrast to that of phenyl 4-nitrophenyl carbonate, which is concerted. This is attributed to a destabilization of the tetrahedral intermediate (T^-) by the change of the thiocarbonyl group by carbonyl as the electrophilic group.

EXPERIMENTAL

Materials

The series of phenols employed were purified by distillation or recrystallization. All the thionocarbonates were obtained as previously reported: **1**,^[29] **2**,^[29] **3**,^[30] **4**^[31] and **5**.^[31]

Kinetics

The reactions were followed spectrophotometrically (300–600 nm) by monitoring the corresponding 4-nitrophenoxide or 4-nitrobenzenethiolate anions by means of a Hewlett-Packard 8453 instrument. The reactions were studied in 44 wt% ethanol–water, at 25.0 ± 0.1 °C, and an ionic strength of 0.2 mol dm^{-3} (maintained with KCl). Borate buffers were used in some reactions. The reactions were started by injection of a substrate stock solution in acetonitrile (10 μl) into the solution of phenoxide ion in 44 wt% ethanol–water (2.5 ml) in the spectrophotometric cell. The initial substrate concentration was $5 \times 10^{-5} \text{ mol dm}^{-3}$. At least a 10-fold excess of total phenol (the anion plus its conjugate acid) over the substrate was employed in all reactions.

Pseudo-first-order rate coefficients (k_{obs}) were found in all cases. These were obtained by means of the kinetic software of the spectrophotometer, after at least four half-lives, except for the slowest reactions (2,3,4,5,6-pentafluorophenol with thionocarbonates **2–5**), where the initial rate method was used.^[1,32]

Determination of pK_a

The pK_a values for the phenols were determined spectrophotometrically by the reported method.^[33] The experimental conditions used were the same as those for the kinetic measurements (44 wt% ethanol–water, 25.0 ± 0.1 °C and ionic strength 0.2 mol dm^{-3} maintained with KCl). The pK_a values obtained for 4-nitrophenol and 4-nitrobenzenethiol were 7.5 and 4.5, respectively. The pK_a values found for the series of phenols employed in this work are shown in Table 1.

Product studies

In the reactions of thiolcarbonates **1** and **2**, 4-nitrobenzenethiolate ion was identified as one of the reaction products. In the reactions of thionocarbonates **3–5**, 4-nitrophenoxide anion was identified as one of the products. This was achieved by comparison of the

UV–Vis spectra after completion of these reactions with those of authentic samples of 4-nitrobenzenethiolate or 4-nitrophenoxide, under the same reaction conditions.

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