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# Effect of substitution of oxygen by sulfur in the nonleaving group of a carbonate: kinetics of the phenolysis and benzenethiolysis of *S*-methyl aryl thiocarbonates

## Enrique A. Castro, Margarita Aliaga and José G. Santos*

Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 6094411, Chile

ABSTRACT: The phenolysis and benzenethiolysis of *S*-methyl 4-nitrophenyl thiocarbonate (**1**) and *S*-methyl 2,4-dinitrophenyl thiocarbonate (**2**) in water are studied kinetically. The Brønsted plots (log $k_N$ *versus* nucleophile basicity) are linear for all reactions. The Brønsted slopes for **1** and **2** are, 0.51 and 0.66 (phenolysis) and 0.55 and 0.70 (benzenethiolysis), respectively. These values suggest a concerted mechanism for these reactions, as found in the corresponding carbonates. Namely, substitution of *O*Me by *S*Me in the nonleaving group does not change the mechanism. Copyright © 2007 John Wiley & Sons, Ltd.
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KEYWORDS: phenolysis; benzenethiolysis; kinetics; thiocarbonates

## INTRODUCTION

Although there have been some studies on the kinetics and mechanisms of the phenolysis of thioesters[1,2] and thiocarbonates,[1,3] the benzenethiolysis of thiocarbonates has attracted less attention.[4] The latter report investigates the kinetics of the benzenethiolyses of alkyl aryl carbonates and *O*-alkyl *S*-aryl thiocarbonates, and discusses the effect of changing the oxygen atom in the leaving group by sulfur. Nevertheless, to our knowledge, there are no reports in the literature on the benzenethiolysis and phenolysis of thiocarbonates where the change of the oxygen atom of a carbonate by sulfur is in the nonleaving group.

In this work, we examine the kinetics and mechanisms of the phenolysis and benzenethiolysis of *S*-methyl 4-nitrophenyl and *S*-methyl 2,4-dinitrophenyl thiocarbonates (**1** and **2**, respectively). By comparison of these reactions with the phenolysis and benzenethiolysis of the corresponding *O*-methyl carbonates (**3** and **4**),[4,5] the effect of substitution of *O*-methyl by *S*-methyl as the nonleaving group will be assessed. Other goal is to

evaluate the effect of the nucleophile (phenoxide *versus* benzenethiolate) on the kinetics and mechanism of these reactions.
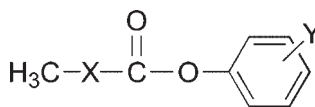


**1** : X = S ; Y = 4-NO$_2$
**2** : X = S ; Y = 2,4-(NO$_2$)$_2$
**3** : X = O ; Y = 4-NO$_2$
**4** : X = O ; Y = 2,4-(NO$_2$)$_2$

## RESULTS AND DISCUSSION

For all the reactions, pseudo-first-order coefficients ($k_{obs}$) were obtained (under nucleophile excess). The experimental conditions of the reactions and the values of $k_{obs}$ are shown in Tables 1–4.

The rate law obtained for all the reactions studied is given by Eqns (1) and (2), where P, S and ArX$^-$ represent the product (either 4-nitrophenoxide or 2,4-dinitrophenoxide anions), the substrate and a substituted phenoxide (X = O) or benzenethiolate (X = S) nucleophile, respectively; $k_0$ is

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

**Table 1.** Experimental conditions and $k_{obs}$ values for the phenolysis of $S$-methyl 4-nitrophenyl thiocarbonate (**1**)[a]

| Phenoxide substituent | pH | $F_N$[b] | $10^3[ArOH]_{tot}$[c]/mol · dm$^{-3}$ | $10^5 k_{obs}$ s$^{-1}$ | no. of runs |
|---|---|---|---|---|---|
| 4-OCH3 | 10.0 | 0.33 | 8.87–35.5 | 171–386 | 6 |
|  | 10.3 | 0.50 | 3.56–35.6 | 77.1–594 | 6 |
|  | 10.6 | 0.67 | 3.71–37.1 | 88.2–846 | 6 |
| H | 9.6 | 0.33 | 1.91–19.1 | 6.59–44.0 | 7 |
|  | 9.9 | 0.50 | 1.96–19.6 | 8.94–70.2 | 7 |
|  | 10.2 | 0.67 | 1.93–19.3 | 7.02–119 | 7 |
| 3-CN | 8.3 | 0.33 | 1.54–15.4 | 1.62–15.5 | 7 |
|  | 8.6 | 0.50 | 1.32–13.2 | 3.65–26.8 | 6 |
|  | 8.9 | 0.67 | 3.31–13.2 | 9.47–32.4 | 6 |
| 4-CN | 7.5 | 0.33 | 1.73–17.3 | 1.51–3.69 | 7 |
|  | 7.8 | 0.50 | 2.02–20.2 | 1.37–5.55 | 6 |
|  | 8.1 | 0.67 | 1.51–15.1 | 1.55–5.90 | 7 |
| 2,6-F$_2$ | 7.5 | 0.7152 | 5.97–50.7 | 2.07–7.71 | 7 |
|  | 8.7[d] | 0.9755 | 6.36–63.6 | 1.58–12.2 | 7 |
|  | 9.3[d] | 0.9937 | 6.36–63.6 | 3.02–12.5 | 7 |
| 2,3,4,5,6-F$_5$ | 8.5[d] | 1.0 | 1.52–15.2 | 0.126–0.464 | 7 |
|  | 9.0[d] | 1.0 | 1.41–14.1 | 0.453–0.678 | 6 |
|  | 9.5[d] | 1.0 | 1.63–16.3 | 0.739–1.12 | 6 |

[a] In aqueous solution, at 25.0 °C, ionic strength 0.2 mol · dm$^{-3}$ (KCl).
[b] Fraction of free phenoxide.
[c] Concentration of total phenol (free phenoxide plus conjugate acid).
[d] Borate buffer 0.02 mol · dm$^{-3}$.

the rate coefficient for hydrolysis and $k_N$ is the rate coefficient either for phenolysis or benzenethiolysis of the substrate.

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

$$k_{obs} = k_0 + k_N[ArX^-] \qquad (2)$$

The value of $k_0$ was much lower than that of $k_N[ArX^-]$ in Eqn (2), except for the slow reactions of 2,3,4,5,6-pentafluorophenol and 2,3,4,5,6-pentafluorobenzenethiol with both substrates and those of thiolcarbonate **1** with 2,6-difluorophenol, where the $k_N[ArX^-]$ term in Eqn (2) was also small. The values of $k_N$ for all reactions were obtained as the slopes of the linear plots of $k_{obs}$ *versus* [ArX$^-$], and were found to be pH independent. These $k_N$

**Table 2.** Experimental conditions and $k_{obs}$ values for the phenolysis of $S$-methyl 2,4-dinitrophenyl thiocarbonate (**2**)[a]

| Phenoxide substituent | pH | $F_N$[b] | $10^3[ArOH]_{tot}$[c]/mol · dm$^{-3}$ | $10^3 k_{obs}$/s$^{-1}$ | no. of runs |
|---|---|---|---|---|---|
| 4-OCH$_3$ | 10.0 | 0.33 | 3.55–35.5 | 4.04–22.5 | 6 |
|  | 10.3 | 0.50 | 3.56–35.6 | 3.14–29.9 | 7 |
|  | 10.6 | 0.67 | 3.71–37.1 | 4.24–38.5 | 7 |
| H | 9.6 | 0.33 | 1.91–16.3 | 0.339–1.66 | 6 |
|  | 9.9 | 0.50 | 1.96–19.6 | 0.415–2.97 | 7 |
|  | 10.2 | 0.67 | 4.83–19.3 | 1.59–4.07 | 6 |
| 3-CN | 8.3 | 0.33 | 1.54–13.1 | 0.078–0.831 | 6 |
|  | 8.6 | 0.50 | 1.32–13.2 | 0.211–1.54 | 6 |
|  | 8.9 | 0.67 | 1.32–13.2 | 0.254–2.03 | 6 |
| 4-CN | 7.5 | 0.33 | 1.73–17.3 | 0.0504–0.29 | 6 |
|  | 7.8 | 0.50 | 3.78–15.1 | 0.0995–0.397 | 6 |
|  | 8.1 | 0.67 | 1.51–15.1 | 0.0376–0.538 | 6 |
| 2,6-F$_2$ | 6.8 | 0.33 | 5.55–47.2 | 0.073–0.690 | 6 |
|  | 7.1 | 0.50 | 5.61–47.7 | 0.118–0.932 | 6 |
|  | 7.5 | 0.715 | 5.97–50.7 | 0.064–1.18 | 7 |
| 2,3,4,5,6-F$_5$ | 8.5[d] | 1.0 | 1.52–15.2 | 0.022–0.063 | 7 |
|  | 9.0[d] | 1.0 | 1.41–14.1 | 0.0173–0.064 | 6 |
|  | 9.5[d] | 1.0 | 1.63–16.3 | 0.044–0.102 | 7 |

[a] In aqueous solution, at 25.0 °C, ionic strength 0.2 mol · dm$^{-3}$ (KCl).
[b] Fraction of free phenoxide.
[c] Concentration of total phenol (free phenoxide plus conjugate acid).
[d] Borate buffer 0.02 mol · dm$^{-3}$.

**Table 3.** Experimental conditions and $k_{obs}$ values for the benzenethiolysis of S-methyl 4-nitrophenyl thiocarbonate (**1**)[a]

| Benzenethiolate substituent | pH | $F_N$[b] | $10^3[ArSH]_{tot}$[c]$/mol \cdot dm^{-3}$ | $10^5 k_{obs}/s^{-1}$ | no. of runs |
|---|---|---|---|---|---|
| H | 6.5 | 0.557 | 2.45–9.80 | 9.98–138 | 6 |
|  | 7.0 | 0.799 | 0.980–9.80 | 16.5–168 | 7 |
| 4-Cl | 5.7 | 0.33 | 0.184–1.44 | 0.264–5.27 | 6 |
|  | 6.0 | 0.50 | 0.179–1.28 | 0.359–9.97 | 6 |
|  | 6.3 | 0.67 | 0.179–1.28 | 2.43–10.5 | 6 |
| 3-Cl | 7.0[d] | 0.969 | 0.429–3.45 | 2.76–30.0 | 6 |
|  | 7.5[d] | 0.99 | 0.429–2.15 | 6.20–20.4 | 6 |
| 2,4-F2 | 6.5[d] | 1 | 0.534–5.34 | 3.40–32.8 | 6 |
|  | 6.6[d] | 1 | 0.958–9.58 | 7.78–48.5 | 6 |
|  | 6.9[d] | 1 | 0.534–4.54 | 5.54–22.5 | 5 |
| 2,3,4,5,6-F5 | 7.0[d] | 1 | 0.525–1.87 | 0.0317–0.0854 | 5 |
|  | 7.3[d] | 1 | 0.375–1.50 | 0.0332–0.0786 | 5 |
|  | 7.6[d] | 1 | 0.375–1.87 | 0.0403–0.0888 | 6 |

[a] In aqueous solution, at 25.0°C, ionic strength $0.2 \, mol \cdot dm^{-3}$ (KCl).
[b] Fraction of free benzenethiolate.
[c] Concentration of total benzenethiol (free benzenethiolate plus conjugate acid).
[d] Buffer phosphate $0.01 \, mol \cdot dm^{-3}$.

**Table 4.** Experimental conditions and $k_{obs}$ values for the benzenethiolysis of S-methyl 2,4-dinitrophenyl thiocarbonate (**2**)[a]

| Benzenethiolate substituent | pH | $F_N$[b] | $10^3[ArSH]_{tot}$[c]$/mol \cdot dm^{-3}$ | $10^3 k_{obs}/s^{-1}$ | No. of runs |
|---|---|---|---|---|---|
| H | 6.0 | 0.285 | 0.98–8.33 | 4.80–63.5 | 6 |
|  | 6.5 | 0.557 | 2.45–8.33 | 6.36–99.9 | 5 |
|  | 7.0 | 0.799 | 0.98–8.33 | 8.59–172 | 6 |
| 4-Cl | 5.7 | 0.33 | 0.184–1.44 | 0.290–3.54 | 6 |
|  | 6.0 | 0.50 | 0.179–1.28 | 0.317–3.84 | 6 |
|  | 6.3 | 0.67 | 0.179–1.02 | 0.354–4.08 | 6 |
| 3-Cl | 5.8 | 0.67 | 0.862–8.62 | 5.13–38.9 | 5 |
|  | 7.0[d] | 0.969 | 0.429–2.15 | 9.70–20.4 | 5 |
|  | 7.5[d] | 0.99 | 0.429–4.74 | 9.92–42.6 | 6 |
| 2,4-F2 | 6.5[d] | 1 | 0.534–5.34 | 5.74–36.8 | 6 |
|  | 6.9[d] | 1 | 1.33–5.34 | 6.91–35.3 | 6 |
| 2,3,4,5,6-F5 | 7.0[d] | 1 | 0.525–2.10 | 0.0304–0.108 | 5 |
|  | 7.3[d] | 1 | 0.375–1.87 | 0.0226–0.0994 | 6 |
|  | 7.6[d] | 1 | 0.375–2.10 | 0.0249–0.104 | 7 |

[a] In aqueous solution, at 25.0°C, ionic strength $0.2 \, mol \cdot dm^{-3}$ (KCl).
[b] Fraction of free benzenethiolate.
[c] Concentration of total benzenethiol (free benzenethiolate plus conjugate acid).
[d] Buffer phosphate $0.01 \, mol \cdot dm^{-3}$.

values are shown in Tables 5 and 6, together with the $pK_a$ values of the series of nucleophiles employed.

Figure 1 shows the Brønsted-type plots obtained with the values of $k_N$ and $pK_a$ in Tables 5 and 6 (measured under the same experimental conditions).

The Brønsted-type plots for the reactions of the two thiocarbonates, **1** and **2**, are linear (Figure 1), with slopes ($\beta$) $0.51 \pm 0.06$ and $0.66 \pm 0.06$, respectively, for phenolysis, and $0.55 \pm 0.05$ and $0.70 \pm 0.1$, respectively, for benzenethiolysis.

The values of the Brønsted slopes found for the title reactions are in accordance with those obtained in the concerted phenolysis of 2,4-dinitrophenyl acetate ($\beta = 0.57$)[6] and 4-chloro-2-nitrophenyl acetate ($\beta = 0.64$).[7]

They are also in agreement with those found in the concerted phenolysis of 3-nitrophenyl, 4-nitrophenyl, and 3,4-dinitrophenyl formates ($\beta = 0.64$, 0.51, and 0.43, respectively)[8] and the corresponding acetates ($\beta = 0.66$, 0.59, and 0.53, respectively)[8], and phthalic and maleic anhydrides ($\beta = 0.45$ and 0.56, respectively).[9] The Brønsted slopes exhibited by the reactions under investigation are also similar to those found in the concerted benzenethiolysis of ethyl 2,4-dinitrophenyl dithiocarbonate ($\beta = 0.66$),[10] ethyl 2,4,6-trinitrophenyl dithiocarbonate ($\beta = 0.66$),[10] and methyl 2,4-dinitrophenyl thionocarbonate ($\beta = 0.58$).[10] Therefore, the $\beta$ values obtained in the phenolysis and benzenethiolysis of the two thiolcarbonates studied in this work suggest that these

**Table 5.** Values of $pK_a$ for the phenols and $k_N$ values for the reactions of phenoxides with 4-nitrophenyl (**1**) and 2,4-dinitrophenyl (**2**) S-methyl thiocarbonates[a]

| Phenoxide substituent | $pK_a$ | $10^2 k_N/s^{-1} \cdot mol^{-1} \cdot dm^3$ | |
|---|---|---|---|
| | | **1** | **2** |
| 4-OCH$_3$ | 10.3 | $30.7 \pm 0.8$ | $150 \pm 5$ |
| H | 9.9 | $8.8 \pm 0.4$ | $31 \pm 2$ |
| 3-CN | 8.6 | $3.6 \pm 0.1$ | $23 \pm 1$ |
| 4-CN | 7.8 | $0.41 \pm 0.04$ | $5.2 \pm 0.1$ |
| 2,6-F$_2$ | 7.1 | $0.19 \pm 0.01$ | $3.4 \pm 0.3$ |
| 2,3,4,5,6-F$_5$ | 5.3 | $0.020 \pm 0.003$ | $0.34 \pm 0.01$ |

[a] Both the $pK_a$ and $k_N$ values were determined in aqueous solution, at 25.0°C, ionic strength 0.2 mol $\cdot$ dm$^{-3}$ (KCl).

**Table 6.** Values of $pK_a$ for the benzenethiols and $k_N$ values for the reactions of benzenethiolates with 4-nitrophenyl (**1**) and 2,4-dinitrophenyl (**2**) S-methyl thiocarbonates[a]

| Benzenethiolate substituent | $pK_a$ | $10^2 k_N/s^{-1} \cdot mol^{-1} \cdot dm^3$ | |
|---|---|---|---|
| | | **1** | **2** |
| H | 6.4 | $21.9 \pm 2.3$ | $2370 \pm 160$ |
| 4-Cl | 6.0 | $13.9 \pm 0.9$ | $645 \pm 37$ |
| 3-Cl | 5.5 | $8.6 \pm 0.6$ | $507 \pm 70$ |
| 2,4-F$_2$ | 4.9 | $5.2 \pm 0.3$ | $669 \pm 35$ |
| 2,3,4,5,6-F$_5$ | 2.7 | $0.0334 \pm 0.0027$ | $4.37 \pm 0.19$ |

[a] Both the $pK_a$ and $k_N$ values were determined in aqueous solution, at 25.0°C, ionic strength 0.2 mol $\cdot$ dm$^{-3}$ (KCl).

reactions are ruled by a concerted mechanism. This is shown in the Scheme (X = O or S, Y = 4-nitro or 2,4-dinitro).



**1** : Y = 4-NO$_2$
**2** : Y = 2,4-(NO$_2$)$_2$          (X = O or S)
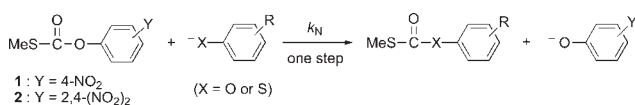
Clearly, the magnitude of $\beta$ is not sufficient to validate the concerted mechanism.[11] If the mechanism for the phenolysis of **1** were stepwise the $pK_a$ value for the center
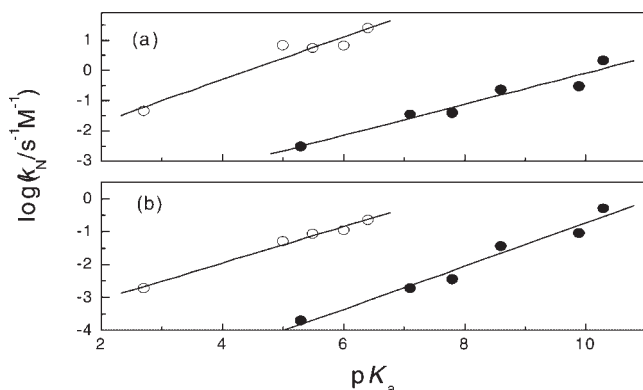


**Figure 1.** Brønsted-type plots obtained in the phenolysis (●) and benzenethiolysis (○) of (a) S-methyl 2,4-dinitrophenyl carbonate (**2**) and (b) S-methyl 4-nitrophenyl carbonate (**1**), in aqueous solution, 25.0 ± 0.1 °C, ionic strength 0.2 mol $\cdot$ dm$^{-3}$ (KCl)

of the Brønsted curvature ($pK_a^0$) would be 7.1 (the $pK_a$ of 4-nitrophenol). The absence of the Brønsted break is a clear indication that this mechanism is not stepwise but concerted.[11] On the other hand, if the reaction of **2** were stepwise the predicted $pK_a^0$ value would be 4.1 (the $pK_a$ of 2,4-dinitrophenol), which is outside the $pK_a$ range studied. Nevertheless, although the Brønsted break cannot be observed, the concerted nature of this reaction can be deduced from the fact that the putative tetrahedral intermediate formed in this reaction should be even more unstable (in view of the better leaving group involved) than that formed in the phenolysis of **1**.

For the benzenethiolysis of 2 the magnitude of the Brønsted slope ($\beta = 0.70$) is near the lower limit of the Brønsted slopes found in stepwise aminolyses of similar substrates when the breakdown to products of the zwitterionic tetrahedral intermediate (T$^\pm$) is the rate-determining step. For instance, Brønsted slope values of 0.8 or slightly lower have been reported for the stepwise aminolysis of 2,4-dinitrophenyl acetate and 1-acetoxy-4-methoxypyridinium ion.[12]

Nevertheless, the $\beta$ value for the benzenethiolysis of **2** is also near the upper limit found for concerted reactions. In fact, linear Brønsted plots with slope values similar or greater than 0.7 have been obtained for the concerted phenolysis of 4-nitrophenyl and 4-formylphenyl acetates ($\beta = 0.75$ and 0.79, respectively).[7]

The above analysis indicates that the benzenethiolysis of **2** is in the borderline between concerted and stepwise mechanisms. Nevertheless, we are more inclined toward

the concerted process as shown in the Scheme (Y = 2,4-(NO$_2$)$_2$, X = S) for the following reasons: (i) If the mechanism of this reaction were stepwise, the p$K$a$^0$ value would be ca. 4 (the p$K_a$ of 2,4-dinitrophenol). This is due to the fact that there is no much difference between the leaving abilities of 2,4-dinitrophenoxide and 2,4-dinitrobenzenethiolate from the anionic tetrahedral intermediate.[2a,4] The lack of a Brønsted break for the benzenethiolysis of **2**, covering a p$K_a$ range 2.7–6.4, indicates that this mechanism is not stepwise. (ii) The instability of the putative anionic tetrahedral intermediate that would be formed if the reaction were stepwise would be very high due to the great compression brought about by the two sulfur atoms attached to the anionic tetrahedral intermediate.

The value of the Brønsted slope for the benzenethiolysis of **1** ($\beta = 0.55$) also suggests a concerted mechanism (Scheme, Y = 4-NO$_2$, X = S). This can be confirmed by the following reasoning: If these mechanisms were stepwise a Brønsted break at p$K_a^0$ ca. 7 would be observed (near the p$K_a$ of 4-nitrophenol, see discussion above). Although this value is outside the p$K_a$ range of the nucleophiles employed, it can be concluded that if the break occurred at this p$K_a$, the rate-determining step for the experimental p$K_a$ range (2.7–6.4) would be the breakdown of the putative T$^-$ to products. The value of the Brønsted slope found ($\beta = 0.55$) is too small compared with those obtained for stepwise mechanisms when breakdown of the anionic tetrahedral intermediate is rate-limiting ($\beta = 0.8$–1.1).[2a,12]

## Phenolysis *versus* Thiolysis

Figure 1 shows a comparison of the Brønsted plots of the nucleophilic rate constants for the benzenethiolysis and phenolysis of thiocarbonates **1** and **2**. It can be observed that in both cases benzenethiolysis is faster than phenolysis toward a carbonyl carbon within the p$K_a$ range studied. A similar result was found in the same reactions of 2,4-dinitrophenyl and 2,4,6-trinitrophenyl methyl carbonates,[4,5] S-(2,4-dinitrophenyl) and S-(2,4,6-trinitrophenyl) ethyl thiocarbonates,[3,4] 4-nitrophenyl acetate[2a] and 4-nitrophenyl formate.[2b] This was explained by the softer character of the sulfur nucleophile, compared with the oxygen nucleophile, which favors the binding of the former to the relatively soft carbonyl carbon.[13] This can be confirmed by the fact that benzenenethiolates show an additional rate enhancement, relative to isobasic phenoxide ions, toward 4-nitrophenyl thiolacetate, which has a softer electrophilic group than that of the corresponding carbonate.[2a]

## Carbonates vs. Thiocarbonates

It has been found that the phenolyses of methyl 4-nitrophenyl and methyl 2,4-dinitrophenyl carbonates

(**3** and **4**, respectively) are driven by a concerted mechanism,[5] as are the phenolyses of **1** and **2** (this work). This indicates that substitution of SMe by OMe as the 'nonleaving' group of the substrates does not change the reaction mechanism.

Comparison of the nucleophilic rate constants ($k_N$) between the phenolysis of thiocarbonates **1** and **2** (this work) and the phenolysis of the corresponding carbonates (**3** and **4**),[5] shows that the latter are more reactive (5 to 10-fold) toward phenoxides than thiocarbonates.

The higher reactivity of carbonates than thiocarbonates toward phenoxide anions seems at first sight surprising in view of the stronger electron-withdrawing effect of SMe in a thiocarbonate compared to OMe in the corresponding carbonate,[14] which should result in the carbonyl carbon of the thiocarbonate being more positively charged and therefore more prone to nucleophilic attack by phenoxide, relative to carbonate. The lower $k_N$ values for the phenolysis of thiocarbonates can be attributed to steric hindrance toward phenoxide attack by the bulkier sulfur atom in a thiocarbonate compared to the oxygen atom in the corresponding carbonate. This is also true when the S and O atoms are in the leaving group: the nucleophilic rate constants ($k_N$) for the phenolysis of methyl aryl carbonates are larger than those of the corresponding S-aryl thiocarbonates.[3,5]

Comparison of the nucleophilic rate constants for the benzenethiolysis of **2** (this study) with those for the corresponding carbonate (**4**)[4] shows that the reactivities of these compounds toward benzenethiolates are similar.

In view of the relative soft nature of benzenethiolates, it should be expected a greater reactivity of these nucleophiles toward the carbonyl group of thiocarbonate **2** compared with that of carbonate **4**, since the carbonyl group of a thiocarbonate should be softer than that of a carbonate.[13] Nevertheless, it is likely that this greater affinity is counterbalanced by a greater steric hindrance, toward the attack of benzenethiolate anion, of the sulfur atom in **2**, relative to oxygen in the corresponding carbonate.

## CONCLUSIONS

The reactions of S-methyl 4-nitrophenyl thiocarbonate (**1**), and S-methyl 2,4-dinitrophenyl thiocarbonate (**2**) with a series of phenols and benzenethiols are studied kinetically in water. The Brønsted slopes, together with other evidence suggest a concerted mechanism for these reactions.

By the comparison of the kinetics and mechanisms of these reactions with those of similar reactions, the following conclusions arise: (i) Thiocarbonates **1** and **2** react with phenoxide and benzenethiolate ions through concerted mechanisms. (ii) Substitution of OMe in carbonates by SMe as the nonleaving group does not affect the mechanism. (iii) Benzenethiolates are more

reactive than isobasic phenoxide ions toward both **1** and **2**. (iv) *S*-Methyl thiocarbonates are less reactive than the corresponding carbonates toward phenoxide ions. (v) Thiocarbonate **2** is as reactive as the corresponding carbonate (**4**) toward benzenethiolate ions.

## EXPERIMENTAL

### Materials

The series of phenols employed were purified by distillation or recrystallization. The series of benzenethiols were used as purchased. Thiolcarbonates **1** and **2** were synthesized as described.[15]

### Kinetics

The reactions were followed spectrophotometrically (300–500 nm) by monitoring the corresponding 4-nitrophenoxide or 2,4-dinitrophenoxide anions by means of a Hewlett-Packard 8453 instrument. The reactions were studied in aqueous solutions, at $25.0 \pm 0.1^{\circ}$C, and an ionic strength of $0.2$ mol $\cdot$ dm$^{-3}$ (maintained with KCl). Phosphate and borate buffers were used in some reactions (see Tables 1–4). The reactions were started by injection of a substrate stock solution in acetonitrile ($10\,\mu$l) into the nucleophile aqueous solution (2.5 ml) in the spectrophotometric cell. The initial substrate concentration was $5 \times 10^{-5}$ mol $\cdot$ dm$^{-3}$. A rapid mixer apparatus was used in some of the fastest reactions. At least a 10-fold excess of total phenol or total benzenethiol (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 4 half-lives, except for the slower reactions (**1** with 2,6-difluorophenol, 2,3,4,5,6-pentafluorophenol, 4-chlorobenzenethiol, 2,4-difluorobenzenethiol and 2,3,4,5,6-pentafluorobenzenethiol and those of **2** with 2,3,4,5,6-pentafluorobenzenethiol) where the initial rate method was used.[16]

### Determination of p$K_a$

The p$K_a$ value for 2.4-difluorbenzenethiol was determined spectrophotometrically at 250 nm by the method reported.[17] The experimental conditions used were the same as those for the kinetic measurements ($25.0 \pm 0.1^{\circ}$C and ionic strength $0.2$ mol $\cdot$ dm$^{-3}$ maintained with KCl). The p$K_a$ value found was $4.9 \pm 0.2$.

## Product studies

4-Nitrophenoxide and 2,4-dinitrophenoxide anions were identified as one of the products of the phenolysis and benzenethiolysis of **1** and **2**, respectively. This was achieved by comparison of the UV-vis spectra after completion of these reactions with those of authentic samples of 4-nitrophenol and 2,4-dinitrophenol under the same reaction conditions.

## REFERENCES

1. Castro EA. *Chem. Rev.* 1999; **19**: 3505–3524.
2. (a) Hupe DJ, Jencks WP. *J. Am. Chem. Soc.* 1977; **99**: 451–464; (b) Pohl ER, Wu D, Hupe DJ. *J. Am. Chem. Soc.* 1980; **102**: 2759–2763; (c) Pohl ER, Hupe DJ. *J. Am. Chem. Soc.* 1980; **102**: 2763–2768.
3. Castro EA, Pavez P, Santos JG. *J. Org. Chem.* 1999; **64**: 2310–2313.
4. Castro EA, Pavez P, Santos JG. *J. Org. Chem.* 2003; **68**: 3640–3645.
5. Castro EA, Pavez P, Santos JG. *J. Org. Chem.* 2001; **66**: 3129–3132.
6. Ba-Saif SA, Colthurst M, Waring MA, Williams A. *J. Chem. Soc., Perkin Trans. 2* 1991; 1901–1908.
7. Ba-Saif S, Luthra AK, Williams A. *J. Am. Chem. Soc.* 1989; **111**: 2647–2652.
8. Stefanidis D, Cho S, Dhe-Paganon S, Jencks WP. *J. Am. Chem. Soc.* 1993; **115**: 1650–1656.
9. Andrés GO, de Rossi RH. *J. Org. Chem.* 2005; **70**: 1445–1449.
10. Castro EA, Pavez P, Santos JG. *J. Org. Chem.* 2003; **68**: 9034–9039.
11. Williams A. *Acc. Chem. Res.* 1989; **22**: 387–392.
12. (a) Jencks WP, Gilchrist M. *J. Am. Chem. Soc.* 1968; **90**: 2622–2637; (b) Satterthwait AC, Jencks WP. *J. Am. Chem. Soc.* 1974; **96**: 7018–7031.
13. (a) Pearson RG. *J. Chem. Educ.* 1968; **45**: 581–587; (b) Pearson RG. *J. Org. Chem.* 1989; **54**: 1423–1430.
14. Hansch C, Leo A, Taft RW. *Chem. Rev.* 1991; **91**: 165–195.
15. Castro EA, Aliaga M, Santos JG. *J. Org. Chem.* 2004; **69**: 6711–6714.
16. Ba-Saif S, Luthra AK, Williams A. *J. Am. Chem. Soc.* 1987; **109**: 6362–6368.
17. Albert A, Serjeant EP. *The Determination of Ionization Constants.* Chapman and Hall: London, UK, 1971; 44.