

Kinetic Study of the Phenolysis of *O*-Methyl and *O*-Phenyl *O*-2,4-Dinitrophenyl Thiocarbonates and *O*-Ethyl 2,4-Dinitrophenyl Dithiocarbonate

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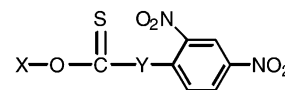
The reactions of a series of phenols with *O*-methyl *O*-2,4-dinitrophenyl thiocarbonate (MDNPTOC), *O*-phenyl *O*-2,4-dinitrophenyl thiocarbonate (PDNPTOC), and *O*-ethyl 2,4-dinitrophenyl dithiocarbonate (EDNPDTC) are studied kinetically in water, at 25.0 °C and an ionic strength of 0.2 M (KCl). All reactions show pseudo-first-order kinetics under an excess of phenol over the substrate, and are first order in phenoxide anion. The reactions of EDNPDTC show a linear Brønsted-type plot of slope $\beta = 0.67$, suggesting a concerted mechanism. On the other hand, the phenolyses of MDNPTOC and PDNPTOC exhibit linear Brønsted-type plots of slopes $\beta = 0.27$ and 0.28, respectively, consistent with stepwise mechanisms where the formation of an anionic tetrahedral intermediate (T^-) is rate determining. By comparison of the kinetics and mechanisms of the reactions under investigation with similar reactions, the following conclusions arise: (i) Substitution of S^- by O^- in the intermediate T^- destabilizes this species. (ii) The change of DNPO in T^- to DNPS also destabilizes this intermediate. (iii) Substitution of MeO by PhO as the nonleaving group of the substrate does not affect the kinetics, probably by a compensation of electronic and steric effects. (iv) The change of an amino group in a tetrahedral intermediate to a phenoxy group destabilizes the intermediate.

Introduction

The kinetics and mechanisms of the phenolysis of esters have been subjected to numerous investigations,¹ but there have been only a few studies on the kinetics of the phenolysis of carbonates,² thioesters,³ thiolcarbonates,⁴ and thionocarbonates.⁵ The phenolysis of carbonates and thiolcarbonates is ruled by concerted mechanisms,^{2,4} but the phenolyses of *O*-methyl *O*-4-nitrophenyl and *O*-bis(4-nitrophenyl) thiocarbonates were shown to be stepwise.⁵ For the latter reactions biphasic Brønsted-type plots were obtained, with breaks (pK_a^0) at pK_a 7.1, which were explained by the formation of an anionic

tetrahedral intermediate (T^-) and a change in the rate-determining step, from T^- breakdown to T^- formation with the increase of the phenoxide basicity.

To extend our kinetic investigations on the phenolysis of thiocarbonyl compounds, in this work we examine the mechanisms of the phenolyses of *O*-methyl and *O*-phenyl *O*-2,4-dinitrophenyl thiocarbonates (MDNPTOC and PDNPTOC, respectively) and of *O*-ethyl 2,4-dinitrophenyl dithiocarbonate (EDNPDTC).



MDNPTOC (X = Me, Y = O)
 PDNPTOC (X = Ph, Y = O)
 EDNPDTC (X = Et, Y = S)

Our goal is to evaluate the effect of the electrophilic (CO vs CS), leaving, and nonleaving groups on the kinetics and mechanism, by comparing the title reactions between them and with the phenolysis of similar carbonates and thiocarbonates.

Experimental Section

Materials. The series of phenols employed were purified by distillation or recrystallization. EDNPDTC was synthesized as described.⁶

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PDNPTOC was synthesized by a modification of literature procedures,^{7–9} as follows: To a solution of 2,4-dinitrophenol (0.3 g, 1.6 mmol) dissolved in dichloromethane (20 mL) in a Schlenk round-bottomed flask was added pyridine in 40% excess, slowly under nitrogen atmosphere. The solution was rapidly transferred to a compensation funnel, under nitrogen. In another Schlenk round-bottomed flask, *O*-phenyl chlorothioformate (0.22 mL) was dissolved in anhydrous dichloromethane (20 mL) under nitrogen. The compensation funnel was attached to the flask and the 2,4-dinitrophenoxide solution added dropwise with stirring. The mixture was left overnight with stirring under nitrogen at ambient temperature. The reaction mixture was washed with a saturated NH_4HSO_4 solution and then with water. The organic layer was dried with MgSO_4 and filtered and the solvent was evaporated off. The product was purified by column chromatography (silica gel, chloroform/hexane 70/30). The pure product, PDNPTOC, melted at 106–108 °C and was identified as follows:

^1H NMR (200 MHz, CDCl_3) δ 7.2–7.5 (m, 5H), 7.64 (d, 1H, $J = 8.9$ Hz), 8.61 (dd, 1H, $J = 2.7, 8.9$ Hz), 9.07 (d, 1H, $J = 8.9$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 191.9, 153.5, 150.2, 145.7, 141.3, 130.0, 129.6, 127.4, 127.3, 122.2, 121.4; IR (KBr) 1347, 1537 (C–NO₂), 1294 (C=S) cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_8\text{N}_2\text{O}_6\text{S}$: C, 48.75; H, 2.52; N, 8.75; S, 10.01. Found: C, 48.89; H, 2.46; N, 8.53; S, 9.77.

MDNPTOC was prepared as described above for PDNPTOC, but using *O*-methyl chlorothioformate.⁹ It melted at 75.6–76.0 °C, and was identified as follows:

^1H NMR (200 MHz, CDCl_3) δ 4.22 (s, 3H), 7.53 (d, 1H, $J = 8.9$ Hz), 8.56 (dd, 1H, $J = 2.7, 8.9$ Hz), 8.99 (d, 1H, $J = 8.9$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 193.0, 150.1, 150.2, 145.5, 141.4, 129.4, 127.4, 122.0, 61.7; IR (KBr) 1346, 1538 (C–NO₂), 1308 (C=S) cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_6\text{N}_2\text{O}_6\text{S}$: C, 37.21; H, 2.32; N, 10.85; S, 12.40. Found: C, 36.83; H, 2.10; N, 10.58; S, 12.35.

O-Bis(phenyl) thiocarbonate⁸ (one of the products in the reaction of phenol with PDNPTOC), *O*-methyl *O*-phenyl thiocarbonate⁷ (one of the products in the reaction of phenol with MDNPTOC), and *O*-ethyl *O*-phenyl thiocarbonate¹⁰ (one of the products in the reaction of phenol with EDNPDT) were prepared as reported.

Kinetic Measurements. These reactions were followed spectrophotometrically (300–500 nm) by monitoring the corresponding 2,4-nitrophenoxide or 2,4-dinitrobenzenethiolate anions. The rate constants were determined at 400 (reactions of MDNPTOC and EDNPDT) and 360 nm (PDNPTOC). The reactions were studied in aqueous solutions, at 25.0 ± 0.1 °C, and an ionic strength of 0.2 M (maintained with KCl). At least a 10-fold excess of total phenol (phenoxide anion plus phenol) over the substrate was employed in all reactions.

Pseudo-first-order rate coefficients (k_{obsd}) 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 slowest reaction (EDNPDT with pentafluorophenol) where the initial rate method was used.¹¹

The experimental conditions of the reactions and the k_{obsd} values are shown in Tables 1–3.

Product Studies. 2,4-Dinitrophenoxide anion was identified as one of the products in the phenolysis of MDNPTOC and PDNPTOC, and 2,4-dinitrobenzenethiolate anion as one of the products in the reactions of EDNPDT. This was achieved by comparison of the UV–vis spectra after completion of these reactions with those of authentic samples of 2,4-

TABLE 1. Experimental Conditions and k_{obsd} Values for the Phenolysis of *O*-Methyl *O*-2,4-Dinitrophenyl Thiocarbonate (MDNPTOC)^a

phenoxide substituent	pH	F_N^b	$10^3[\text{ArOH}]_{\text{tot}}/M^c$	$10^3k_{\text{obsd}}/s^{-1}$	no. of runs
4-OCH ₃	10.0	0.33	6.0–80.0	2.22–32.6	7
	10.3	0.50	6.0–60.0	3.89–35.3	6
	10.6	0.67	6.0–80.0	6.75–70.0	7
H	9.6	0.33	6.0–80.0	1.77–21.0	7
	9.9	0.50	6.0–80.0	2.20–27.0	7
	10.2	0.67	6.0–80.0	3.44–39.2	7
3-CN	8.3	0.33	2.0–25.0	0.25–3.51	7
	8.6	0.50	2.0–25.0	0.43–5.42	7
	8.9	0.67	2.0–25.0	0.62–6.94	7
4-CN	7.5	0.33	0.80–10.0	0.092–1.10	7
	7.8	0.50	0.80–10.0	0.134–1.60	7
	8.1	0.67	0.80–10.0	0.162–2.10	7
2,6-F ₂	6.8	0.33	6.0–80.0	0.25–4.86	7
	7.1	0.50	6.0–80.0	0.62–7.71	6
	7.4	0.67	6.0–60.0	0.66–7.20	6
2,3,4,5,6-F ₅	5.0	0.33	6.0–60.0	0.124–0.830	6
	5.3	0.50	6.0–60.0	0.161–1.28	6
	5.6	0.67	6.0–80.0	0.222–2.10	7

^a In aqueous solution, at 25.0 °C, ionic strength 0.2 M (KCl).

^b Fraction of free phenoxide. ^c Concentration of total phenol (free phenoxide plus conjugate acid).

TABLE 2. Experimental Conditions and k_{obsd} Values for the Phenolysis of *O*-Phenyl *O*-2,4-Dinitrophenyl Thiocarbonate (PDNPTOC)^a

phenoxide substituent	pH	F_N^b	$10^3[\text{ArOH}]_{\text{tot}}/M^c$	$10^3k_{\text{obsd}}/s^{-1}$	no. of runs
4-OCH ₃	10.0	0.33	8.0–60.0	6.58–31.4	5
	10.3	0.50	6.0–75.0	6.35–37.8	7
	10.6	0.67	8.0–75.0	8.26–63.0	6
H	9.6	0.33	2.0–25.0	0.420–5.30	7
	9.9	0.50	2.0–25.0	0.874–8.15	7
	10.2	0.67	2.5–25.0	1.10–13.0	6
3-CN	8.3	0.33	6.5–80.0	0.813–9.89	7
	8.6	0.50	6.5–80.0	0.980–16.7	7
	8.9	0.67	6.5–60.0	1.81–17.9	6
4-CN	7.5	0.33	6.5–80.0	0.156–5.12	7
	7.8	0.50	6.5–60.0	0.671–7.20	6
	8.1	0.67	6.5–60.0	0.500–8.74	5
2,6-F ₂	6.8	0.33	25–80.0	0.968–3.80	4
	7.1	0.50	6.5–80.0	0.580–5.88	6
	7.4	0.67	6.5–80.0	0.500–6.38	7
2,3,4,5,6-F ₅	5.0	0.33	8.0–80.0	0.128–1.25	6
	5.3	0.50	8.0–80.0	0.170–2.00	6
	5.6	0.67	8.0–80.0	0.200–2.77	6

^a In aqueous solution, at 25.0 °C, ionic strength 0.2 M (KCl).

^b Fraction of free phenoxide. ^c Concentration of total phenol (free phenoxide plus conjugate acid).

dinitrophenol and 2,4-dinitrobenzenethiol, under the same reaction conditions.

In the reactions of MDNPTOC, PDNPTOC, and EDNPDT with phenoxide anion, *O*-methyl *O*-phenyl thiocarbonate, *O*-bis(phenyl) thiocarbonate, and *O*-ethyl *O*-phenyl thiocarbonate, respectively, were found as the other product of these reactions. All these products were identified by HPLC, using authentic samples as standards. HPLC conditions: column, Eurospher C-18 (10 cm, 7 μm); eluent, acetonitrile/water 70/30; isocratic mode, 0.7 mL/min.

Results and Discussion

The rate law obtained for all the reactions studied is given by eqs 1 and 2, where P, S, and ArO^- represent the product (either 2,4-dinitrophenoxide or 2,4-dinitrobenzenethiolate anions), a substrate, and a substituted

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TABLE 3. Experimental Conditions and k_{obsd} Values for the Phenolysis of *O*-Ethyl 2,4-Dinitrophenyl Dithiocarbonate (EDNPDTc)^a

phenoxide substituent	pH	F_N^b	$10^3[\text{ArOH}]_{\text{tot}}/M^c$	$10^3 k_{\text{obsd}}/s^{-1}$	no. of runs
4-OCH ₃	10.0	0.33	6.0–80.0	12.9–118	6
	10.3	0.50	10.0–80.0	28.9–183	5
	10.6	0.67	10.0–80.0	32.6–253	5
H	9.4	0.26	6.0–60.0	1.80–14.3	5
	9.7	0.41	6.0–60.0	3.01–25.9	5
	10.0	0.58	6.0–60.0	4.03–35.3	5
3-Cl	8.7	0.33	6.0–60.0	1.34–9.42	5
	9.0	0.50	6.0–60.0	1.74–13.6	5
	9.3	0.67	6.0–60.0	2.11–17.9	5
4-CN	7.5	0.33	10.0–90.0	0.25–1.92	5
	7.8	0.50	10.0–90.0	0.39–2.80	5
	8.1	0.67	10.0–90.0	0.53–3.45	5
2,3,4,5,6-F ₅	6.5 ^d	0.94	10.0–85.0	0.0010–0.111	5
	6.8 ^d	0.97	10.0–85.0	0.0019–0.111	5
	7.0 ^d	0.98	10.0–85.0	0.0021–0.0994	5

^a In aqueous solution, at 25.0 °C, ionic strength 0.2 M (KCl).

^b Fraction of free phenoxide. ^c Concentration of total phenol (free phenoxide plus conjugate acid). ^d In the presence of phosphate buffer 0.005 M.

TABLE 4. Values of pK_a of Phenols and k_N for the Phenolysis of *O*-Methyl *O*-2,4-Dinitrophenyl Thiocarbonate (MDNPOTC), *O*-Phenyl *O*-2,4-Dinitrophenyl Thiocarbonate (PDNPOTC), and *O*-Ethyl 2,4-Dinitrophenyl Dithiocarbonate (EDNPDTc)^a

phenoxide substituent	pK_a	$10^2 k_N/s^{-1} M^{-1}$		
		MDNPOTC	PDNPOTC	EDNPDTc
4-OCH ₃	10.3	124 ± 4	130 ± 3	451 ± 2
H	9.9	71 ± 3	71 ± 1	97 ± 4
3-Cl	9.0			43 ± 1
3-CN	8.6	46 ± 1	41.0 ± 0.5	
4-CN	7.8	23 ± 1	31.0 ± 0.3	5.9 ± 0.2
2,6-F ₂	7.1	13.0 ± 0.5	19.0 ± 0.5	
2,3,4,5,6-F ₅	5.3	5.0 ± 0.1	4.0 ± 0.1	0.13 ± 0.01

^a Both the pK_a and k_N values were determined in aqueous solution, at 25.0 °C, ionic strength 0.2 M (KCl).

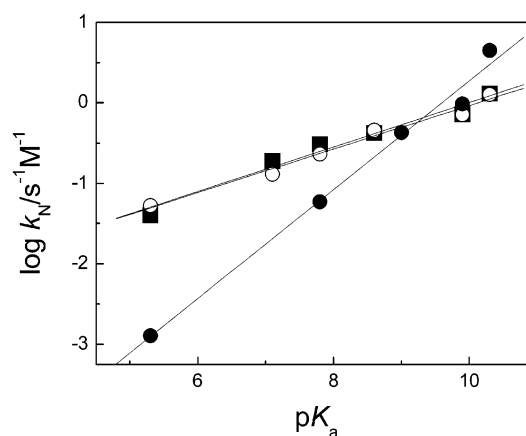
phenoxide nucleophile, respectively, and k_0 and k_N are the rate coefficients for hydrolysis and phenolysis of the substrates, respectively.

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

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

The value of k_0 was much lower than those of $k_N[\text{ArO}^-]$ in eq 2, except in the slow reactions of pentafluorophenol with the three substrates, where the phenolysis term in eq 2 was also small. The rate coefficient k_0 measures the attack of water and/or that of OH⁻ to the substrate, depending on the pH values. In the particular case of the reactions of EDNPDTc with pentafluorophenoxide, where phosphate buffer was used, the k_0 values also include the catalysis by the buffer (presumably base-catalyzed hydrolysis). The values of k_N for all reactions were obtained as the slope of linear plots of k_{obsd} vs [ArO⁻]. The k_N values were found to be pH independent. These k_N values are shown in Table 4, together with the pK_a values of the series of phenols employed.

Figure 1 shows the Brønsted-type plots obtained with the values of k_N and pK_a in Table 4 (measured under the same experimental conditions).

**FIGURE 1. Brønsted-type plots for the phenolysis of MDNPOTC (○), PDNPOTC (■), and EDNPDTc (●) in water, at 25.0 °C, ionic strength 0.2 M (KCl). The slopes (β) are 0.27, 0.28, and 0.67, respectively.**

The Brønsted-type plots for the phenolysis of the two thionocarbonates, MDNPOTC and PDNPOTC, are linear (see Figure 1), with slopes (β) 0.27 and 0.28, respectively. These values are in accordance with those found in the stepwise phenolyses of *O*-methyl *O*-4-nitrophenyl and *O*-bis(4-nitrophenyl) thiocarbonates, when formation of the anionic tetrahedral intermediate (T⁻) is the rate-determining step.⁵ The β values also agree with those found in the reactions of pyridines with alkyl aryl carbonates,¹² secondary alicyclic amines (SAA) with methyl 4-nitrophenyl carbonate,¹³ quinuclidines and SAA with diaryl carbonates,^{14,15} pyridines and SAA with aryl thiolacetates,¹⁶ SAA with diaryl thionocarbonates,¹⁷ and SAA and pyridines with dithiocarbonates,^{6,18} when formation of the zwitterionic tetrahedral intermediate (T[±]) is rate limiting ($\beta = 0.1–0.3$).

Therefore, the β values obtained in the phenolysis of the two thionocarbonates studied in this work suggest that these reactions are ruled by a stepwise mechanism, where the formation of an anionic tetrahedral intermediate (T⁻) is rate limiting (Scheme 1, R = methyl or phenyl, DNP = 2,4-dinitrophenyl).

If the mechanism for the phenolysis of the above thionocarbonates is stepwise the pK_a value for the center of the Brønsted curvature (pK_a^0) should be 4.1 (the pK_a of 2,4-dinitrophenol). This value lies outside the pK_a range of the series of phenols employed, preventing, therefore, the observation of the Brønsted break. Nevertheless, the predicted pK_a^0 value of 4.1 for a stepwise mechanism confirms that for the reactions of the thiono-

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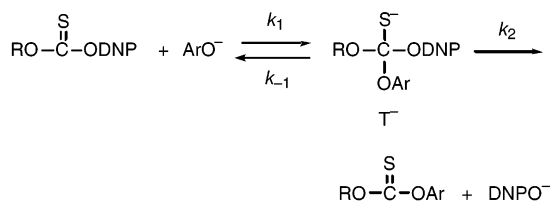
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SCHEME 1

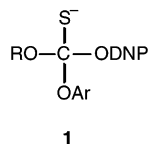


carbonates with the phenols employed in this work the rate-determining step is the formation of the intermediate T^- in Scheme 1.

The phenolysis of *O*-methyl *O*-4-nitrophenyl thiocarbonate shows a biphasic Brønsted plot with $\text{p}K_{\text{a}}^0 = 7.1$, which is the $\text{p}K_{\text{a}}$ of 4-nitrophenol, a clear indication that this mechanism is stepwise.⁵ The fact that the formation of the intermediate T^- is rate limiting for the reactions of the same phenols with MDNPTOC is in accordance with the previous finding, since 2,4-dinitrophenoxide is a better nucleofuge from T^- than 4-nitrophenoxide from the corresponding intermediate, and this should decrease the $\text{p}K_{\text{a}}^0$ value for the phenolysis of MDNPTOC compared to that for the reactions of the same phenols with the mononitro derivative.

The similar k_{N} values exhibited by the phenolysis of MDNPTOC and PDNPTOC (Table 4 and Figure 1) is noteworthy. Larger k_{N} values for the latter reactions could be expected if only electronic effects were considered, since the phenoxy group is more electron withdrawing than methoxy inductively ($\sigma_{\text{I}} = 0.37$ and 0.29 , respectively) and less electron donating by resonance ($\sigma_{\text{R}} = -0.40$ and -0.56 , respectively).¹⁹ Nevertheless, the phenoxy group is bulkier than methoxy and should offer a greater steric hindrance to nucleophilic attack than methoxy; therefore, the electronic advantage of the phenoxy group should be compensated by its steric disadvantage.

It has been found that the phenolysis of methyl 2,4-dinitrophenyl carbonate is driven by a concerted mechanism;^{2a} in contrast, the phenolysis of MDNPTOC shows a stepwise path (this work). This suggests that substitution of S^- in intermediate **1** ($\text{R} = \text{Me}$) by O^- destabilizes this intermediate to the point of mechanistic change.

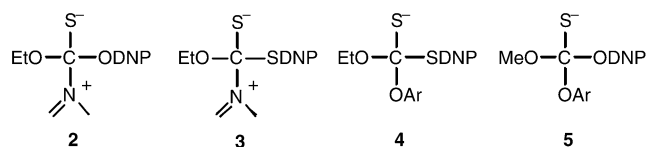


The above result is in agreement with the fact that the reactions of SAA with 2,4-dinitrophenyl and 2,4,6-trinitrophenyl *O*-ethyl thiolcarbonates are concerted,²⁰ whereas the reactions of the same amines with 2,4-dinitrophenyl and 2,4,6-trinitrophenyl *O*-ethyl dithiocarbonates are stepwise.⁶ Moreover, the phenolyses of bis(4-nitrophenyl) carbonate⁵ and methyl 4-nitrophenyl carbonate^{2a} are ruled by concerted mechanisms, in opposition to the same reactions of *O*-bis(4-nitrophenyl) thiocarbonate and *O*-

methyl *O*-4-nitrophenyl thiocarbonate, which show stepwise mechanisms.⁵ The destabilization of a tetrahedral intermediate by substitution of S^- by O^- has been explained by the greater ability of O^- in the intermediate to form a double bond and expel a nucleofuge, compared to S^- , due to a stronger π -bonding energy of the carbonyl group relative to thiocarbonyl.²¹

The Brønsted-type plot for the phenolysis of EDNPDTC is linear, with slope $\beta = 0.67$ (Figure 1), which is in accordance with a concerted mechanism. Analogous β values have been obtained for the concerted phenolyses of 2,4-dinitrophenyl and 2,4,6-trinitrophenyl *O*-ethyl thiolcarbonates,⁴ 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl methyl carbonates,^{2a} diaryl carbonates,^{2c,5} aryl acetates,^{1b,d,e} and acetic anhydride.^{1d}

The value of $\beta = 0.67$ for the phenolysis of EDNPDTC is near the lower limit of the β values found for stepwise reactions when breakdown of the tetrahedral intermediate to products is the rate-determining step ($\beta = 0.8-1.0$).^{6,7,12-14,16,18,22} Nevertheless, the stepwise mechanism can be ruled out on the following grounds: For the pyridinolyses of *O*-ethyl *O*-2,4-dinitrophenyl thiocarbonate and EDNPDTC stepwise mechanisms were found, as evidenced by biphasic Brønsted plots with the $\text{p}K_{\text{a}}$ values at the curvature center ($\text{p}K_{\text{a}}^0$) of 6.8 and 6.9, respectively.^{7,18} This suggests that the leaving abilities of 2,4-dinitrophenoxide (DNPO^-) and 2,4-dinitrobenzenethiolate (DNPS^-) from the corresponding zwitterionic tetrahedral intermediates (**2** and **3**, respectively) are similar.¹⁸ This is due to the fact that the lower basicity of DNPS^- than DNPO^- ($\text{p}K_{\text{a}}$ of the corresponding phenols are 3.4 and 4.1, respectively)^{16b} is compensated by an intrinsic lower nucleofugality of an ArS^- group compared to an *isobasic* ArO^- group.²³ On the other hand, for the stepwise phenolysis of MDNPTOC the predicted Brønsted break ($\text{p}K_{\text{a}}^0$) is 4.1 (see above). If the phenolysis of EDNPDTC were stepwise, and assuming that DNPS^- has a similar leaving ability as DNPO^- from the corresponding anionic tetrahedral intermediates (**4** and **5**, respectively), the value of $\text{p}K_{\text{a}}^0$ for the hypothetical stepwise mechanism of EDNPDTC would be ca. 4.1. This analysis assumes that the change of EtO to MeO in an anionic tetrahedral intermediate does not alter the rate microcoefficients k_{-1} and k_2 (shown in Scheme 1) involved in the stepwise process. This is reasonable since these rate microcoefficients are not influenced by the change of the above substituents in a zwitterionic tetrahedral intermediate.⁷ Therefore, if the phenolysis of EDNPDTC were stepwise the Brønsted β value would be similar to those found for the phenolysis of the thionarbonates ($\beta = 0.27, 0.28$), i.e., formation of the tetrahedral intermediate would be rate limiting. This is true even if DNPS^- leaves **4** faster than DNPO^- from **5** (see below). Since for the phenolysis of EDNPDTC the Brønsted β value is 0.67, the stepwise mechanism for this reaction can be excluded.

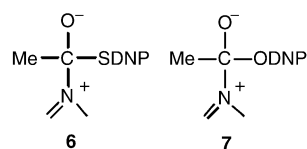


The above mechanistic change, from stepwise for the phenolysis of MDNPTOC to concerted for that of EDN-

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PDTC, is surprising on the basis that DNPO⁻ and DNPS⁻ leave the zwitterionic tetrahedral intermediates **2** and **3**, respectively, at similar rates. Nevertheless, it is possible that DNPS⁻ leaves faster than DNPO⁻ from the corresponding anionic tetrahedral intermediates **4** and **5**, respectively. In fact, DNPS⁻ is a better nucleofuge than DNPO⁻ from the tetrahedral intermediates (**6** and **7**)



formed in the pyridinolysis of the corresponding thiolacetate and acetate, as judged by the pK_a^0 values of 6.6 and 7.3 found in the reactions of 2,4-dinitrophenyl thiolacetate^{16b} and 2,4-dinitrophenyl acetate,^{12b} respectively. Another possibility is that the anionic intermediate (**4**) formed in the phenolysis of EDNPDTC is more unstable thermodynamically than that (**5**) formed in the same reactions of MDNPTOC, the former reaction bypassing therefore intermediate **4** and choosing the less energetic concerted path.

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The aminolysis (SAA) of EDNPDTC follows a stepwise mechanism, as evidenced by the biphasic Brønsted-type plot obtained.⁶ The fact that the phenolysis of the same substrate is concerted (this work) is in agreement with the destabilization of zwitterionic tetrahedral intermediates by substitution of an amino group by ArO. Examples of this type of destabilization are the stepwise reactions of SAA with (i) 4-nitrophenyl and 2,4-dinitrophenyl acetates,^{22,24} compared with the concerted phenolyses of these compounds,^{1d,e} (ii) *O*-ethyl 4-nitrophenyl thiolcarbonate,²⁵ and (iii) *O*-phenyl and *O*-4-nitrophenyl chlorothioformates,²⁶ in contrast to the concerted phenolyses of the same substrates.^{4,27}

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Supporting Information Available: Experimental conditions, values of the concentrations of total substituted phenols, and k_{obsd} for the reactions of SAA with MDNPTOC (Table S1), PDNPTOC (Table S2), and EDNPDTC (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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