

Kinetics and Mechanism of the Benzenethiolysis of *O*-Ethyl *S*-(2,4-Dinitrophenyl) and *O*-Ethyl *S*-(2,4,6-Trinitrophenyl) Dithiocarbonates and *O*-Methyl *O*-(2,4-Dinitrophenyl) Thiocarbonate

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Reactions of *O*-ethyl 2,4-dinitrophenyl dithiocarbonate (EDNPDTDC), *O*-ethyl 2,4,6-trinitrophenyl dithiocarbonate (ETNPDTDC), and *O*-methyl *O*-(2,4-dinitrophenyl) thiocarbonate (MDNPTOC) with a series of benzenethiolate anions in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M (KCl), are subjected to a kinetic investigation. Under excess benzenethiolate, these reactions obey pseudo-first-order kinetics and are first order in benzenethiolate. Nonetheless, similar reactant concentrations were used in the reactions of 4-nitrobenzenethiolate anion with the ethyl trinitrophenyl ester (ETNPDTDC), which showed overall second-order kinetics. The nucleophilic rate constants (k_N) are pH independent, except those for the reactions of ETNPDTDC with the X-benzenethiolates with X = H, 4-Cl, and 3-Cl, which increase as pH decreases. The Brønsted-type plots ($\log k_N$ vs pK_a of benzenethiols) are linear with slopes $\beta = 0.66$ for the reactions of both ethyl dinitrophenyl ester (EDNPDTDC) and ethyl trinitrophenyl ester (ETNPDTDC) and $\beta = 0.58$ for those of the thiocarbonate ester (MDNPTOC). For the benzenethiolysis of MDNPTOC and EDNPDTDC, no breaks were found in the Brønsted-type plots at pK_a 4.1 and 3.4, respectively, consistent with concerted mechanisms. Benzenethiolysis of the ethyl trinitrophenyl ester (ETNPDTDC) should also be concerted in view of the even more unstable tetrahedral "intermediate" that would have been formed had this reaction been stepwise. ETNPDTDC is more reactive toward benzenethiolate anions than EDNPDTDC due to the better leaving group involved in the former substrate. The k_N values found for the reactions of EDNPDTDC with benzenethiolates are larger than those obtained for the concerted reactions of the same substrate with isobasic phenoxide anions. This is explained by Pearson's "hard and soft acids and bases" principle. The concerted mechanism for the benzenethiolysis of MDNPTOC, in contrast to the stepwise mechanism found for the phenolysis of this substrate, is attributed to the greater kinetic instability of the hypothetical tetrahedral "intermediate" formed in the former reaction, due to the greater nucleofugality of ArS^- compared with an isobasic ArO^- . Benzenethiolates are more reactive toward MDNPTOC and EDNPDTDC than the corresponding carbonate and thiocarbonate, respectively. This is also in accordance with the HSAB principle, since benzenethiolates are relatively soft bases that prefer to bind to a relatively soft thiocarbonyl center rather than a relatively hard carbonyl center.

Introduction

Although there is abundant literature on the kinetics and mechanisms of the phenolysis of esters and thioesters,¹⁻⁴ and there have been some reports on the same

reactions of carbonates and thiocarbonates,^{5,6} there have been only a few investigations on the kinetics and mechanism of the benzenethiolysis of esters and thioesters^{2,7} and only one on the latter reactions of carbonates and thiocarbonates.⁸ Furthermore, we are not aware of any reports on the kinetics of the benzenethiolysis of thiocarbonyl compounds.

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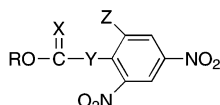
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We have found that the phenolysis of ethyl *S*-(2,4-dinitrophenyl) dithiocarbonate (EDNPDTDC) is concerted,⁶ whereas the corresponding reaction of methyl 2,4-dinitrophenyl thionocarbonate (MDNPTOC) is governed by a stepwise mechanism.⁶ This difference of mechanism was explained by the greater nucleofugality of 2,4-dinitrobenzenethiolate than 2,4-dinitrophenoxide from the corresponding hypothetical tetrahedral intermediates, which kinetically destabilizes the former "intermediate".⁶

Recently, we have described the benzenethiolysis of methyl 2,4-dinitrophenyl and methyl 2,4,6-trinitrophenyl carbonates (MDNPC and MTNPC, respectively) and of ethyl *S*-(2,4-dinitrophenyl) and ethyl *S*-(2,4,6-trinitrophenyl) thiolcarbonates (EDNPTC and ETNPTC, respectively).⁸ These reactions were found to be concerted on the basis of the linear Brønsted plots obtained and the absence of a break at the expected pK_a for a hypothetical stepwise mechanism.⁸

To extend our kinetic studies on the reactions of benzenethiolates, in the present work we carry out a kinetic investigation of the benzenethiolysis of EDNPDTDC, ETNPDTDC, and MDNPTOC. The following are the goals of this work. (i) To examine the influence of the leaving group of the substrate on the kinetics and mechanism, by comparing the three reactions series. (ii) To assess the effect of the nucleophile, by comparison of the title reactions with the phenolysis of the same substrates.⁶ (iii) To evaluate the change of carbonyl to thiocarbonyl as an electrophilic center by comparison of the reactions under study with the benzenethiolysis of carbonates and thiolcarbonates.⁸ (iv) To compare the kinetics of the back reactions of the benzenethiolysis of the dinitrophenyl thionocarbonate with the phenolysis of the dinitrophenyl dithiocarbonate.⁶



EDNPDTDC (R = Et, X = Y = S, Z = H)
 ETNPDTDC (R = Et, X = Y = S, Z = NO₂)
 MDNPTOC (R = Me, X = S, Y = O, Z = H)
 MDNPC (R = Me, X = Y = O, Z = H)
 MTNPC (R = Me, X = Y = O, Z = NO₂)
 EDNPTC (R = Et, X = O, Y = S, Z = H)
 ETNPTC (R = Et, X = O, Y = S, Z = NO₂)

Experimental Section

Materials. The series of benzenethiols were used as purchased. The substrates: EDNPDTDC,⁹ ETNPDTDC,⁹ and MDNPTOC⁶ were synthesized as described previously.

Kinetic Measurements. These were performed spectrophotometrically (diode array) in the range 300–500 nm by following the appearance of the corresponding 2,4-dinitrophenoxide or 2,4-dinitro- or 2,4,6-trinitro-benzenethiolate anions. The reactions were carried out 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 benzenethiol over the substrate was used, except in the reaction of 4-nitrobenzenethiolate with ETNPDTDC. For this reaction (followed at 400 nm), equimolar concentrations (1 × 10⁻⁵ M) of the reagents were used and second-order kinetics were obtained.

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TABLE 1. Experimental Conditions and k_{obsd} Values for the Reactions of Benzenethiolate Anions with *O*-Ethyl 2,4-Dinitrophenyl Dithiocarbonate^a

benzenethiolate substituent	pH	10 ³ [ArSH] _{tot} ^b (M)	10 ³ k_{obsd} (s ⁻¹)	no. of runs
none	4.5 ^c	0.10–0.80	0.83–13.2	5
	5.0 ^c	0.10–1.0	3.40–26.0	4
	5.5 ^c	0.10–1.0	4.00–64.0	6
4-chloro	4.5 ^c	0.10–1.0	0.99–6.11	5
	5.0 ^c	0.10–1.0	1.91–29.0	4
	5.5 ^c	0.10–1.0	6.30–69.0	5
3-chloro	8.0 ^d	0.10–1.0	40.0–181	4
	8.5 ^d	0.10–1.0	33.0–202	5
	9.0 ^d	0.10–1.0	28.0–183	5
2,3,4,5,6-pentafluoro	4.5 ^c	1.0–10	2.30–24.0	4
	5.0 ^c	1.0–10	2.90–27.0	4
	5.5 ^c	1.0–10	2.95–29.0	4

^a In aqueous solution, at 25.0 °C and an ionic strength of 0.2 M (KCl). ^b Total concentration of substituted benzenethiol (acid plus conjugate base). ^c In the presence of acetate buffer 0.01 M. ^d In the presence of borate buffer 0.01 M.

TABLE 2. Experimental Conditions and k_{obsd} Values for the Reactions of Benzenethiolate Anions with *O*-Ethyl 2,4,6-Trinitrophenyl Dithiocarbonate^a

benzenethiolate substituent	pH	10 ³ [ArSH] _{tot} ^b (M)	10 ² k_{obsd} (s ⁻¹)	no. of runs
none	2.5 ^c	0.10–1.0	28.0–80.0	6
	3.0 ^c	0.10–0.80	50.0–98.0	4
	3.5 ^c	0.10–1.0	62.0–114	5
4-chloro	2.5 ^c	0.10–0.80	32.0–98.5	4
	3.0 ^c	0.10–0.80	62.0–149	5
	3.5 ^c	0.10–1.0	76.2–156	6
3-chloro	2.5 ^c	0.10–1.0	15.0–63.3	6
	3.0 ^c	0.10–1.0	17.9–92.2	4
	3.5 ^c	0.10–1.0	21.1–104	5
4-nitro ^d	4.5 ^e	0.01		10
2,3,4,5,6-pentafluoro	4.5 ^e	0.25–1.0	12.7–57.0	5
	5.0 ^e	0.25–1.0	20.0–67.0	5
	5.5 ^e	0.40–1.0	46.0–83.0	4

^a In aqueous solution, at 25.0 °C and an ionic strength of 0.2 M (KCl). ^b Total concentration of substituted benzenethiol (acid plus conjugate base). ^c In the presence of citrate buffer 0.01 M. ^d For this reaction (carried out with an equimolar concentration of reactants), second-order kinetics were obtained. ^e In the presence of acetate buffer 0.01 M.

The initial concentration of the substrates was (0.5–3) × 10⁻⁵ M, and pseudo-first-order rate coefficients (k_{obsd}) were found, except in the particular case mentioned above. The experimental conditions of the reactions and the k_{obsd} values obtained are shown in Tables 1–3.

Product Studies. For the benzenethiolysis of MDNPTOC, EDNPDTDC, and ETNPDTDC, one of the products was identified as 2,4-dinitrophenoxide, 2,4-dinitrobenzenethiolate, and 2,4,6-trinitrobenzenethiolate anions, respectively. This was carried out by comparison of the UV–vis spectra after completion of these reactions with those of authentic samples under the same experimental conditions.

In the reactions of EDNPDTDC and ETNPDTDC with benzenethiolate, the other product was identified as *O*-ethyl *S*-phenyl dithiocarbonate (EPDTC) by comparison, through HPLC, of a sample at the end of the reaction with an authentic sample¹⁰ as a standard. HPLC conditions: column, Eurospher C-18 (10 cm, 7 μm); eluant, acetonitrile/water 70/30; isocratic mode, 0.5 mL/min.

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TABLE 3. Experimental Conditions and k_{obsd} Values for the Reactions of Benzenethiolate Anions with *O*-Methyl *O*-(2,4-Dinitrophenyl) Thiocarbonate^a

benzenethiolate substituent	pH	$10^3 [\text{ArSH}]_{\text{tot}}^b$ (M)	$10^3 k_{\text{obsd}}$ (s^{-1})	no. of runs
4-methoxy	6.0 ^c	0.05–1.00	0.88–46.8	6
	6.5 ^c	0.05–0.50	14.2–90.0	5
	7.0 ^c	0.10–1.00	16.1–147	6
4-methyl	8.5 ^d	0.25–2.00	0.90–13.0	6
4-chloro	8.0 ^d	0.10–2.00	3.22–67.5	7
	8.5 ^d	0.25–2.00	11.6–70.1	6
	9.0 ^d	0.25–2.00	12.0–73.5	6
3-chloro	8.5 ^d	0.25–5.00	5.15–110	6
	9.0 ^d	0.25–5.00	7.55–117	6
2,3,4,5,6-pentafluoro	8.0 ^d	0.80–10.0	0.528–6.98	6
	8.5 ^d	0.80–10.0	0.564–7.07	6
	9.0 ^d	0.80–10.0	0.60–7.30	6

^a In aqueous solution, at 25.0 °C and an ionic strength of 0.2 M (KCl). ^b Total concentration of substituted benzenethiol (acid plus conjugate base). ^c In the presence of phosphate buffer 0.01 M. ^d In the presence of borate buffer 0.01 M.

Results and Discussion

The kinetic equation obtained for the title reactions, with the exception of the reaction of 4-nitrobenzenethiolate with ETNPDTTC, is given by eq 1, where P is 2,4-dinitrophenoxide, 2,4-dinitrobenzenethiolate, or 2,4,6-trinitrobenzenethiolate anions, S represents the substrate (MDNPTOC, EDNPDTTC, or ETNPDTTC), and k_{obsd} is the pseudo-first-order rate constant.

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

For these reactions, linear plots of k_{obsd} versus benzenethiolate (ArS^-) concentration were obtained, according to eq 2, where k_0 and k_N are the rate coefficients for hydrolysis and benzenethiolysis of the substrates, respectively. The values of k_0 and k_N were determined as the intercept and slope, respectively, of the linear plots mentioned above.

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

The values of both k_0 and k_N were found to be pH independent, except those for the reactions of ETNPDTTC

with the X-benzenethiolate anions with X = H, 3-Cl, and 4-Cl, which were conducted at low pH values. For the latter reactions, the plots of k_{obsd} vs $[\text{ArS}^-]$ are linear at each pH, showing an increase of the slope with the decrease of the pH value. For these reactions, k_{obsd} can be described by eq 3, where k_N and k_H are the nucleophilic and the acid-catalyzed rate constants, respectively. The same kinetic behavior was observed for the reactions of some benzenethiolates with MTNPC and ETNPDTTC at low pH values.⁸ The values of k_N and k_H found for the reactions in this work, together with the $\text{p}K_a$ values of the substituted benzenethiols,¹¹ are shown in Table 4.

$$k_{\text{obsd}} = k_0 + k_N[\text{ArS}^-] + k_H[\text{ArS}^-][\text{H}^+] \quad (3)$$

Table 4 also includes the k_N value for the reaction of 4-nitrobenzenethiolate with ETNPDTTC, which was determined under second-order conditions. This reaction could not be studied under pseudo-first-order conditions because of the high absorbance of this nucleophile.⁸ The hydrolysis reaction was checked in the absence of 4-nitrobenzenethiolate: no significant reaction was observed during the time the reaction with 4-benzenethiolate is complete. The back reaction was not significant as judged by the good second-order kinetics found. The same behavior was observed for the reactions of this nucleophile with methyl 2,4,6-trinitrophenyl carbonate and ethyl 2,4,6-trinitrophenyl thiolcarbonate.⁸

For the reactions of MDNPTOC and EDNPDTTC with 4-nitrobenzenethiolate ion, the determination of k_N was not possible since the UV-vis spectra of the leaving groups, 2,4-dinitrophenoxide and 2,4-dinitrobenzenethiolate anions, are very similar to that of NPS^- . Even under second-order experimental conditions, the differences in absorbance of the above compounds during the reactions are very small. This was also the case for the reactions of NPS^- with the corresponding dinitro carbonate and thiolcarbonate.⁸

The acid catalysis exhibited by the reactions of some benzenethiolate anions with ETNPDTTC was probably due to the fact that these were the only reactions carried out at low pH (2.5–3.5) values. A similar catalysis was found in the benzenethiolysis of MTNPC and ETNPDTTC,⁸ in the addition of thiol anions to acetaldehyde^{12a} and in the

TABLE 4. Values of $\text{p}K_a$ of Benzenethiols and k_N and Brønsted-Type Equations for the Benzenethiolysis of MDNPTOC, EDNPDTTC, and ETNPDTTC^a

benzenethiolate substituent	$\text{p}K_a$ of benzenethiol	k_N ($\text{s}^{-1} \text{M}^{-1}$)		
		MDNPTOC	EDNPDTTC	ETNPDTTC
4-methoxy	6.5 ^b	199 ± 8		
4-methyl	6.4 ^b	70 ± 2		
none	6.4 ^b		865 ± 35	$(1.7 \pm 0.2) \times 10^{4c}$
4-chloro	6.0 ^b	34 ± 1	307 ± 10	$(1.1 \pm 0.2) \times 10^{4c}$
3-chloro	5.5 ^d	22.7 ± 0.6	172 ± 6	$(6.7 \pm 1.2) \times 10^{3c}$
4-nitro	4.6 ^b			$(1.6 \pm 0.1) \times 10^{3e}$
pentafluoro	2.7 ^f	0.71 ± 0.01	2.7 ± 0.2	61 ± 4
Brønsted-type equation ^g		$-1.76 + 0.58 \text{p}K_a$	$-1.36 + 0.66 \text{p}K_a$	$0.069 + 0.66 \text{p}K_a$

^a Values of k_N in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M (KCl). ^b Values of $\text{p}K_a$ taken from ref 11a, in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M. ^c Values of k_N obtained from eq 3. The values of k_H obtained from this equation for the reactions of ETNPDTTC are $(1.8 \pm 0.2) \times 10^8 \text{ s}^{-1} \text{M}^{-2}$ (benzenethiolate), $(9 \pm 1) \times 10^7 \text{ s}^{-1} \text{M}^{-2}$ (4-chlorobenzenethiolate), and $(1.5 \pm 0.2) \times 10^7 \text{ s}^{-1} \text{M}^{-2}$ (3-chlorobenzenethiolate). ^d Value of $\text{p}K_a$ determined by interpolation of the linear relationship between the $\text{p}K_a$ values measured in aqueous solution, at 25.0 °C and an ionic strength 0.2 M (ref 11a), and the thermodynamic $\text{p}K_a$ values in water at 25.0 °C (ref 11b). ^e Value of k_N measured under second-order conditions (see text). ^f Value of $\text{p}K_a$ measured in aqueous solution at 25.0 °C and an ionic strength of 1.0 M (ref 11c). ^g Log k_N as a function of $\text{p}K_a$ of benzenethiols.

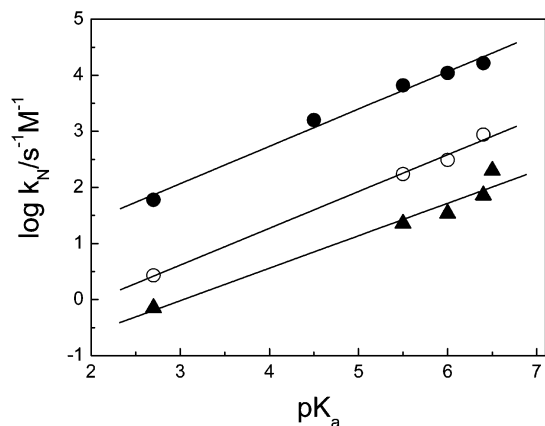


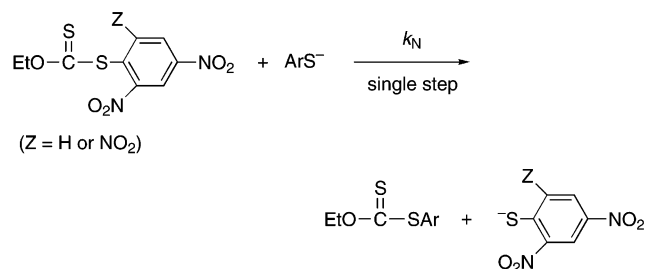
FIGURE 1. Brønsted-type plots obtained for the benzenethiolysis of *O*-ethyl *S*-(2,4,6-trinitrophenyl) dithiocarbonate (●), *O*-ethyl *S*-(2,4-dinitrophenyl) dithiocarbonate (○), and *O*-methyl *O*-(2,4-dinitrophenyl) thiocarbonate (▲) in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M.

reactions of 4-cyanopyridine with 2,4-dinitrophenyl acetate and methyl 2,4-dinitrophenyl carbonate,^{12b} all of which were conducted at low pH values.

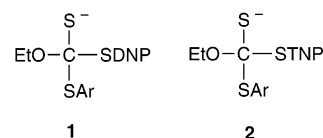
Figure 1 shows the Brønsted-type plots obtained for the benzenethiolysis of MDNPOTC, EDNPOTC, and ETNPOTC, obtained with the k_N and pK_a values in Table 4.

The Brønsted-type plots for EDNPOTC and ETNPOTC are linear with slope (β) values of 0.66 for both, in accordance with concerted mechanisms.^{1,4b,e,5,6,13} Nevertheless, the magnitude of the β value alone is not sufficient to prove a concerted mechanism. Definite proof requires evidence that there is no break in the Brønsted-type plot at the predicted pK_a for a hypothetical stepwise mechanism.¹⁴ If the benzenethiolysis of EDNPOTC were stepwise, the Brønsted plot would have a break centered at a pK_a (pK_a^0) value of 3.4, which is the pK_a of 2,4-dinitrobenzenethiol.¹⁵ At this pK_a , a (hypothetical) substituted benzenethiolate nucleophile (ArS^-) would leave the putative anionic tetrahedral intermediate (**1**) as fast as 2,4-dinitrobenzenethiolate ($DNPS^-$). Since the benzenethiolysis of EDNPOTC shows no break at pK_a 3.4 (Figure 1), the stepwise mechanism can be ruled out for this reaction series.¹⁴ This means that compound **1** is either very unstable or does not exist, the latter situation corresponding to an enforced concerted mechanism.¹⁶ If the putative intermediate **1** is so unstable, the hypothetical intermediate **2** in the benzenethiolysis of ETNPOTC would be even more unstable since 2,4,6-trinitroben-

SCHEME 1



zenethiolate ($TNPS^-$) is a better nucleofuge from **2** than $DNPS^-$ from **1**. Therefore, it is very probable that the benzenethiolysis of ETNPOTC, as well as that of EDNPOTC, would also be driven by a concerted mechanism (shown in Scheme 1).



The substrate ETNPOTC is more reactive toward benzenethiolates than EDNPOTC (Figure 1); this should be due to the presence of a third nitro group in ETNPOTC, which would speed both the attack of the nucleophile and the nucleofugality of the leaving group.

As seen in Figure 1, benzenethiolates react faster with EDNPOTC than with MDNPOTC. This result can be explained by the soft nature of benzenethiolates, which favor the binding to a softer electrophilic center such as the thiocarbonyl group of a dithiocarbonate rather than the harder thiocarbonyl center of a thionocarbonate. This is in agreement with Pearson's "hard and soft acids and bases" (HSAB) principle.¹⁷ The difference of the nonleaving groups (MeO and EtO) of these two substrates should not be an important factor regarding the difference in reactivity of these substrates (see below).¹⁸

With the k_N values obtained for the benzenethiolysis of both dithiocarbonates (Table 4), together with the pK_a values of the benzenethiols as both nucleophiles (Table 4) and nucleofuges (pK_a 3.4 and 1.4 for 2,4-dinitro- and 2,4,6-trinitrobenzenethiols, respectively¹⁵), eq 4 can be obtained by dual regression analysis ($n = 9$, $R^2 = 0.994$). In this equation, $pK_a(N)$ and $pK_a(lg)$ are those corresponding to the nucleophile and leaving group, respectively.

$$\log k_N = 1.13 + 0.66 pK_a(N) - 0.73 pK_a(lg) \quad (4)$$

A double logarithmic plot (not shown) of the k_N values obtained experimentally (Table 4) versus those calculated through eq 4 is linear with unity slope and zero intercept.

The sensitivity of $\log k_N$ to the nucleophile basicity ($\beta_N = 0.66$) is in line with the β_N values found for other concerted mechanisms, as discussed above. On the other hand, the sensitivity of $\log k_N$ to the leaving group basicity ($\beta_{lg} = -0.73$) is in accordance with the β_{lg} values

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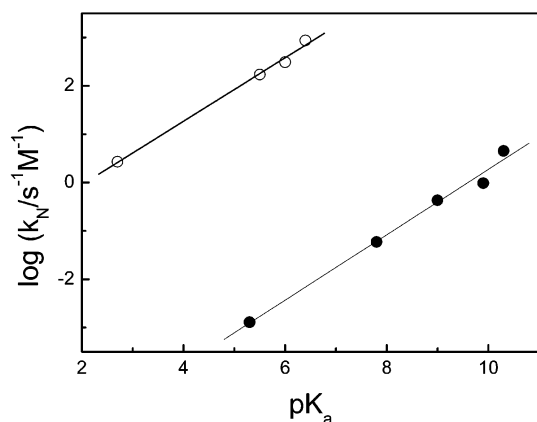
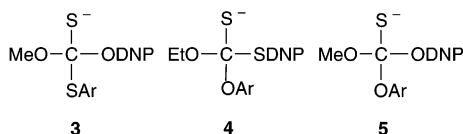


FIGURE 2. Brønsted-type plots obtained for the benzenethiolysis (○, this work) and phenolysis (●, ref 6) of *O*-ethyl 2,4-dinitrophenyl dithiocarbonate, in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M.

obtained for the concerted phenolyses of aryl acetates and aryl formates.^{4e}

The Brønsted-type plot (Figure 1) for the benzenethiolysis of MDNPTOC, obtained with the k_N values and the pK_a of the benzenethiols (Table 4), is linear with a slope of 0.58, also in agreement with a concerted mechanism. Furthermore, there is no break in this Brønsted-type plot near the pK_a of 2,4-dinitrophenol (pK_a 4.1 under the experimental conditions).⁸ If an anionic tetrahedral intermediate (**3**) were formed in these reactions, it would be expected that 2,4-dinitrophenoxide (DNPO⁻) would leave this intermediate as fast as an *isobasic* benzenethiolate (ArS⁻). This is because the greater intrinsic nucleofugality of a given aryloxide, compared to an *isobasic* benzenethiolate,^{7c} is counterbalanced by a greater push exerted by the former to expel an *isobasic* benzenethiolate from the tetrahedral intermediate.^{2a} In fact, for the stepwise thiolysis of 4-nitrophenyl and 2,4-dinitrophenyl acetates, the Brønsted breaks are centered at $pK_a^0 = 7.8$ and 5.0, respectively, which are close to the pK_a values of 4-nitrophenol and 2,4-dinitrophenol, respectively.^{2a} Likewise, for the stepwise thiolysis of 4-nitrophenyl formate and pivalate, the Brønsted breaks are centered at pK_a ca. 7.^{2b} The lack of a Brønsted break at pK_a ca. 4 for the benzenethiolysis of MDNPTOC (Figure 1), confirms that this mechanism is concerted.⁸



On the other hand, the existence of an anionic “intermediate” (**4**) very similar to compound **3** was ruled out for the phenolysis of EDNPDTTC.⁶ The change of MeO to EtO as the nonleaving group should not significantly affect the stability of a tetrahedral intermediate since the above change does not alter the microcoefficients involved in the decomposition of zwitterionic tetrahedral intermediates, for instance, those formed in the pyridinolysis of alkyl aryl thionocarbonates.¹⁸ The concerted phenolysis of EDNPDTTC is the microscopic back reaction of the

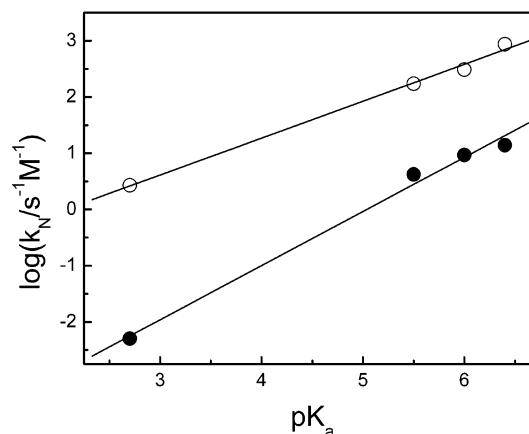


FIGURE 3. Brønsted-type plots obtained for the benzenethiolyses of EDNPDTTC (○, this work) and EDNPTC (●, ref 8), in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M.

benzenethiolysis of MDNPTOC and therefore must have the same mechanism. In conclusion, it is reasonable that intermediate **3** is either very unstable or nonexistent; therefore, the benzenethiolysis of MDNPTOC should be concerted.¹⁴

The phenolysis of MDNPTOC has been found to be stepwise, with rate-determining formation of the anionic tetrahedral intermediate **5**.⁶ This is in contrast to the concerted benzenethiolysis of this compound (this work), which bypasses the highly unstable intermediate **3**. These results indicate that the change of ArO to ArS destabilizes intermediate **5**. This can be attributed to the greater nucleofugality of ArS⁻ from **3**, compared with that of ArO⁻ from **5**, due to the lower basicity of ArS⁻ relative to ArO⁻.

A comparison of the Brønsted-type plots for the concerted benzenethiolysis of EDNPDTTC (this work) and the concerted phenolysis of the same substrate⁶ is shown in Figure 2. As observed, benzenethiolates react faster than *isobasic* phenoxides toward the thiocarbonyl carbon of this substrate. This can be attributed to the softer character of the sulfur nucleophile, relative to the oxygen nucleophile, that would prefer to bind to the relatively soft thiocarbonyl carbon, in accordance to Pearson’s HSAB principle.¹⁷ Benzenethiolates are also better nucleophiles than *isobasic* aryloxides toward the carbonyl group of acetates,^{2a,b} carbonates,⁸ and thiolcarbonates,⁸ despite that these are considered harder centers than thiocarbonyl.¹⁷

The fact that the Brønsted slope for the faster benzenethiolysis of EDNPDTTC ($\beta = 0.66$) is similar to the slower phenolysis of the same compound ($\beta = 0.68$)⁶ is against the reactivity–selectivity principle and the Hammond postulate.¹⁹ Nonetheless, there are many examples of concerted reactions that show anti Hammond behavior.^{8,14,20} We have also found that the fast concerted benzenethiolyses of carbonates and thiolcarbonates⁸ ex-

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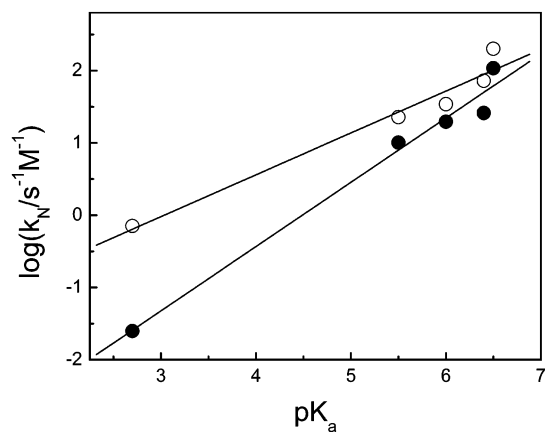


FIGURE 4. Brønsted-type plots obtained for the benzenethiolyses of MDNPTOC (○, this work) and MDNPC (●, ref 8), in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M.

hibit larger β values than the slower concerted phenolysis of the same compounds.^{5a,b}

With the k_N values obtained in this work for the benzenethiolysis of MDNPTOC and EDNPDTTC, together with those found for the same reactions of the corresponding carbonate (MDNPC) and thiolcarbonate (EDNPTC),⁸ a comparison between the four Brønsted-type plots can be made. Figure 3 shows the Brønsted plots for the reactions of EDNPDTTC and EDNPTC, and Figure 4 exhibits those for MDNPTOC and MDNPC.

From Figure 3, it can be observed that benzenethiolates are more reactive toward EDNPDTTC than EDNPTC, whereas Figure 4 shows that these nucleophiles react faster with MDNPTOC than with MDNPC. This clearly indicates that these soft sulfur nucleophiles have a preference toward a soft center such as a thiocarbonyl group over a harder carbonyl group.¹⁷

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