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Kinetics and Mechanism of the Benzenethiolysis of 2,4-Dinitrophenyl and 2,4,6-Trinitrophenyl Methyl Carbonates and *S*-(2,4-Dinitrophenyl) and *S*-(2,4,6-Trinitrophenyl) Ethyl Thiolcarbonates

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The reactions of 2,4-dinitrophenyl and 2,4,6-trinitrophenyl methyl carbonates (DNPC and TNPC, respectively) and *S*-(2,4-dinitrophenyl) and *S*-(2,4,6-trinitrophenyl) ethyl thiolcarbonates (DNPTC and TNPTC, respectively) with a series of benzenethiolate anions were subjected to a kinetic investigation in water, at 25.0 °C, and an ionic strength of 0.2 M (KCl). These reactions obey pseudo-first-order kinetics, under excess of benzenethiolate, and are first order in the latter reactant. However, comparable reactant concentrations were used in the reactions of 4-nitrobenzenethiolate anion with TNPC and TNPTC, which showed second-order kinetics. The nucleophilic rate constants are pH independent, except those for the reactions of TNPC with 4-methoxy- and pentafluorobenzenethiolates, and TNPTC with benzenethiolate and 4-chloro- and 3-chlorobenzenethiolates, which show acid dependence. The Brønsted-type plots for the nucleophilic rate constants are linear with slopes $\beta = 0.9$, 1.0, 0.9, and 0.9 for the reactions of DNPC, TNPC, DNPTC, and TNPTC, respectively. No break in the Brønsted plot was found for the reactions of DNPC and DNPTC at pK_a ca. 4.1 and 3.4, respectively, consistent with concerted mechanisms. TNPC is more reactive toward benzenethiolate anions than DNPC, and TNPTC more than DNPTC due to the better leaving groups involved. Comparison of the kinetic results obtained in this work with those for the concerted phenolysis of the same substrates shows that benzenethiolate anions are better nucleophiles toward carbonates than isobasic phenoxide anions. This is explained by Pearson's "hard and soft acids and bases" principle.

Introduction

There have been many reports in the literature on the kinetics and mechanisms of the phenolysis of esters and thioesters,[1-3] but only a few on the mechanisms of the same reactions of carbonates and thiocarbonates.[4] Concerning the thiolysis of the above compounds, there have been a few studies on the kinetics and mechanism of the reactions of esters and thioesters,[1,5] but none, to our knowledge, on the thiolysis of aryl carbonates or *S*-aryl thiolcarbonates.

We have found that the phenolyses of *S*-(4-nitrophenyl), *S*-(2,4-dinitrophenyl), and *S*-(2,4,6-trinitrophenyl) ethyl thiocarbonates (NPTC, DNPTC, and TNPTC, respectively) are driven by concerted mechanisms.[4a] The phenolyses of 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl methyl carbonates (NPC, DNPC, and TNPC, respectively) were also found to be concerted on the basis of the linear Brønsted-type plots with slopes β ca. 0.5−0.7 obtained.[4b]

To extend our investigations on the mechanisms of the reactions of aryl carbonates, we perform in the present work a kinetic study of the benzenethiolysis of DNPC, TNPC, DNPTC, and TNPTC. The aim of this work is as follows: (i) to assess the influence of the leaving group of the substrate on the kinetics and mechanism, by comparing the title reactions; (ii) to evaluate the effect of the nucleophile, by comparison of the mechanism of the reactions under study with that for the phenolysis of the same substrates;[4a,b] and (iii) to compare the kinetics

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TABLE 1. Experimental Conditions and k_{obsd} Values for the Reactions of Benzenethiolate Anions with 2,4-Dinitrophenyl Methyl Carbonate (DNPC)[a]

benzenethiolate substituent	pH	10^3 [ArSH]$_{tot}$[b]/M	10^3 k_{obsd}/s^{-1}	no. of runs
4-methoxy	6.0[c]	0.10−1.0	2.0−24	5
	6.5[c]	0.10−0.70	6.2−44	4
	7.0[c]	0.050−0.70	5.0 − 52	5
none	6.0[c]	0.50−10	1.4−48	6
	6.5[c]	0.50−10	5.5−96	6
	7.0[c]	0.50−5.0	6.4−72	4
4-chloro	6.4[c]	0.50−10	0.50−120	5
	6.6[c]	0.50−10	2.2−153	6
	7.0[c]	0.50−10	7.6−181	6
3-chloro	8.0[d]	0.25−3.5	1.9−33	5
	8.5[d]	0.25−5.0	2.3−48	6
	9.0[d]	0.25−5.0	2.8−53	6
2,3,4,5,6-pentafluoro	8.0[d]	0.50−10	0.10−0.31	6
	8.5[d]	0.50−10	0.18−0.43	6
	9.0[d]	1.0−10	0.67−0.94	5

[a] In water, at 25.0 °C, ionic strength 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.

TABLE 2. Experimental Conditions and k_{obsd} Values for the Reactions of Benzenethiolate Anions with 2,4,6-Trinitrophenyl Methyl Carbonate (TNPC)[a]

benzenethiolate substituent	pH	10^3 [ArSH]$_{tot}$[b]/M	10^2 k_{obsd}/s^{-1}	no. of runs
4-methoxy	2.5[c]	0.25−1.0	0.80−12	6
	3.0[c]	0.10−0.70	2.4−18	5
	3.5[c]	0.10−0.70	6.5−38	5
4-chloro	3.5[d]	0.25−0.80	7.6−13	4
	4.0[d]	0.25−0.80	14−25	4
	4.5[d]	0.10−0.80	17−66	5
3-chloro	4.0[d]	0.10−0.80	9.2−15	4
	4.5[d]	0.25−1.0	16−41	5
	5.0[d]	0.10−0.60	20−56	4
4-nitro[e]	4.5[d]	0.01		10
2,3,4,5,6-pentafluoro	2.4	1.0−10	1.7−20	5
	2.7	0.50−5.0	0.80−12	4
	3.0	0.40−3.0	1.6−7.8	5

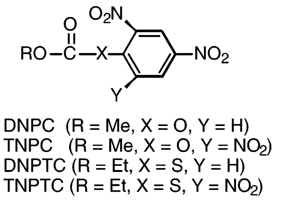
[a] In water, at 25.0 °C, ionic strength 0.2 M (KCl). [b] Total concentration of substituted benzenethiol (acid plus conjugate base). [c] In the presence of citrate buffer 0.01 M. [d] In the presence of acetate buffer 0.01 M. [e] For this reaction (carried out with an equimolar concentration of reactants),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

TABLE 3. Experimental Conditions and k_{obsd} Values for the Reactions of Benzenethiolate Anions with *S*-(2,4-Dinitrophenyl) Ethyl Thiocarbonate (DNPTC)[a]

benzenethiolate substituent	pH	10^3 [ArSH]$_{tot}$[b]/M	10^3 k_{obsd}/s^{-1}	no. of runs
none	8.0[c]	0.50−10.0	6.22−63.3	4
	8.5[c]	0.50−10.0	6.50−65.2	4
	9.0[c]	0.50−10.0	7.71−138	5
4-chloro	8.0[c]	0.10−1.00	1.00−9.49	4
	8.5[c]	0.10−1.00	1.14−9.46	4
	9.0[c]	0.10−1.00	0.58−9.47	4
3-chloro	7.5[c]	0.10−1.00	0.25−3.80	4
	8.5[c]	0.10−1.00	0.45−4.00	4
	9.0[c]	0.10−1.00	0.55−4.60	4
2,3,4,5,6-pentafluoro	4.5[d]	1.00−10.0	0.0074−0.054	4
	5.0[d]	1.00−10.0	0.0073−0.052	4
	5.5[d]	1.00−10.0	0.0065−0.055	4

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

of the back reactions of the benzenethiolyses of the above carbonates with the phenolysis of *S*-aryl ethyl thiolcarbonates.[4a]



Experimental Section

Materials. The benzenethiols were used as purchased. The substrates DNPC,[6a,b] TNPC,[6c] DNPTC,[7a] and TNPTC[7b] were synthesized as previously reported.

Kinetic Measurements. Kinetic measurements were carried out spectrophotometrically in the range 300−500 nm (appearance of the substituted phenoxide or benzenethiolate anions) by means of a diode array spectrophotometer. The reactions were investigated in aqueous solutions, 25.0 ± 0.1 °C, ionic strength 0.2 M (maintained with KCl), and at least a 10-fold excess of total benzenethiol over the substrate was employed, except in the reactions of 4-nitrobenzenethiolate with TNPC and TNPTC. For the latter reactions (followed at 400 nm), an equimolar concentration (1×10^{-5} M) of the reactants was employed and second-order kinetics were obtained.

With the above exceptions, the initial concentration of the substrates was 3×10^{-5} M and pseudo-first-order rate coefficients (k_{obsd}) were found in all cases. The experimental conditions of the reactions and the k_{obsd} values obtained are shown in Tables 1−4.

Product Studies. For the benzenethiolysis of DNPC, TNPC, DNPTC, and TNPTC, one of the products was identified as 2,4-dinitrophenoxide, 2,4,6-trinitrophenoxide 2,4-dinitrobenzenethiolate, and 2,4,6-trinitrobenzenethiolate anions, respectively. The identification was achieved by comparison of the UV−vis spectra after completion of the reactions with those of authentic samples under the same conditions.

Results and Discussion

The rate law obtained for most of the reactions under investigation (the exceptions being the reactions of 4-nitrobenzenethiolate with TNPC and TNPTC) is given by eq 1, where P is 2,4-dinitrophenoxide, 2,4,6-trinitrophenoxide, 2,4-dinitrobenzenethiolate, or 2,4,6-trinitrobenzenethiolate anions, S represents the substrate (DNPC, TNPC, DNPTC, or TNPTC), and k_{obsd} is the pseudo-first-order rate coefficient.

$$\frac{d[P]}{dt} = k_{obsd}[S] \tag{1}$$

For the above reactions, the plots of k_{obsd} against benzenethiolate (ArS$^-$) concentration are linear, according to eq 2, where k_0 and k_N are the rate coefficients for hydrolysis and thiolysis of the substrates, respectively.

$$k_{obsd} = k_0 + k_N[ArS^-] \tag{2}$$

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TABLE 4. Experimental Conditions and k_{obsd} Values for the Reactions of Benzenethiolate Anions with *S*-(2,4,6-Trinitrophenyl) Ethyl Thiocarbonate (TNPTC)[a]

benzenethiolate substituent	pH	10^3 $[ArSH]_{tot}$[b]/M	10^2 k_{obsd}/s^{-1}	no. of runs
none	2.5[c]	0.10−1.00	0.82−4.60	6
	3.0[c]	0.10−1.00	1.80−8.00	5
	3.5[c]	0.10−1.00	2.50−15.4	5
4-chloro	2.5[c]	0.10−1.00	4.80−10.5	6
	3.0[c]	0.10−1.00	4.90−11.2	6
	3.5[c]	0.10−1.00	5.00−9.80	4
3-chloro	2.5[c]	0.10−1.00	2.10−8.20	6
	3.0[c]	0.10−1.00	2.30−9.00	6
	3.5[c]	0.10−1.00	3.00−9.70	6
4-nitro[d]	4.5[e]	0.01		10
2,3,4,5,6-pentafluoro	4.5[e]	1.00−10.0	2.80−14.8	4
	5.0[e]	1.00−10.0	2.90−15.2	4
	5.5[e]	1.00−10.0	3.00−13.8	4

[a] In water, at 25.0 °C, ionic strength 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.

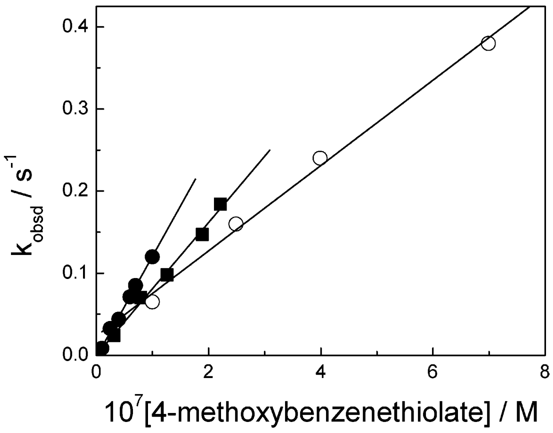

FIGURE 1. Plots of k_{obsd} vs concentration of free 4-methoxybenzenethiolate, obtained in the reaction of this anion with 2,4,6-trinitrophenyl methyl carbonate (TNPC), at pH 2.5 (●), pH 3.0 (■), and pH 3.5 (○).

The values of both the slope (k_N) and the intercept (k_0) are pH independent, except those for the reactions of TNPC with 4-methoxy- and pentafluorobenzenthiolate anions and TNPTC with 4-chloro-, 3-chloro-, and unsubstituted benzenethiolate anions. For these reactions, the plot of k_{obsd} vs $[ArS^-]$ is linear at each pH (see Figure 1 as an example), but the slope increases as the pH decreases. The plot (not shown) of the slopes in Figure 1 vs $[H^+]$ is linear, with slope k_H (the acid-catalyzed rate constant) and intercept k_N (the nucleophilic rate constant). Namely, for these reactions, k_{obsd} behaves kinetically according to eq 3. The values of k_N and k_H in aqueous solution, 25.0 °C, ionic strength 0.2 M are shown in Table 5.

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

The values obtained for the nucleophilic rate constants (k_N in eqs 2 and 3), the acid-catalyzed rate constants (k_H in eq 3), and the pK_a of benzenethiols[8] are shown in Table 5.

Table 5 includes the k_N values obtained for the reactions of 4-nitrobenzenethiolate with TNPC and TNPTC, under second-order conditions. These reactions could not be studied under pseudo-first-order conditions, as in the case of the other benzenethiolates, due to the high absorbance of this nucleophile, which prevented its use in great excess over the substrate. The hydrolysis reaction was checked in the absence of 4-nitrobenzenethiolate: No significant reaction was observed during the time the reaction with benzenethiolate is complete. The back reaction was not significant as indicated by the good second-order kinetics obtained. This is reasonable due to the poor nucleophilicity (and also low concentration) of 2,4,6-trinitrophenoxide or 2,4,6-trinitrobenzenethiolate anions toward the alkyl *S*-(4-nitrophenyl) thiolcarbonates compared to that of 4-nitrobenzenethiolate anion toward TNPC and TNPTC. Therefore, the latter reactions can be completely described by eq 4.

$$RO{-}CO{-}XTNP + NPS^- \rightarrow RO{-}CO{-}SNP + TNPX^- \qquad (4)$$

$$(R = Me, X = O; R = Et, X = S; TNP = 2,4,6\text{-trinitrophenyl}; NP = 4\text{-nitrophenyl})$$

For the reactions of DNPC and DNPTC with 4-nitrobenzenethiolate, the determination of k_N was not possible due to the fact that the UV−vis spectra of the leaving groups, 2,4-dinitrophenoxide and 2,4-dinitrobenzenethiolate anions, are very similar to that of 4-nitrobenzenethiolate. Even under second-order experimental conditions the absorbance differences observed during the reactions are very small.

The acid catalysis found for the reactions of some benzenethiolate anions with TNPC and TNPTC was presumably observed because these were the only reactions carried out at low pH (2.4−3.5) values. It is reasonable to assume that the other reactions would show the same catalysis at low pH values. A similar catalysis was found in the addition of thiol anions to acetaldehyde[9a] and in the reactions of 4-cyanopyridine with 2,4-dinitrophenyl acetate and DNPC.[9b] The much larger k_H value obtained for the reaction of TNPC with 4-methoxybenzenethiolate compared to that for the reaction of the same substrate with the pentafluoro derivative (Table 5) can be attributed to a general-acid catalysis (by the acid form of the citrate buffer) for the former reaction since this was carried out in the presence of external buffer whereas the latter was studied without external buffer. The acid-catalyzed path was not further investigated.

The Brønsted-type plots for the benzenethiolysis of DNPTC and TNPTC, obtained with the k_N values and the pK_a of the benzenethiols (taken from Table 5), are

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TABLE 5. Values of pK_a of Benzenethiols and k_N for the Reactions of Benzenethiolates with Aryl Methyl Carbonates and *S*-Aryl Ethyl Thiolcarbonates[a]

		k_N/s^{-1} M^{-1}	10^{-3} k_N/s^{-1} M^{-1}	k_N/s^{-1} M^{-1}	10^{-3} k_N/s^{-1} M^{-1}
benzenethiolate substituent	pK_a of benzenethiol	DNPC	TNPC	DNPTC	TNPTC
4-methoxy	6.5[b]	108 ± 7	500 ± 80[c]		
none	6.4[b]	26 ± 1	–	13.9 ± 0.4	108 ± 5[c]
4-chloro	6.0[b]	19.7 ± 0.4	23.3 ± 0.7	9.3 ± 0.2	6.8 ± 4.4[c]
3-chloro	5.5[d]	10.1 ± 0.3	4.3 ± 0.2	4.2 ± 0.4	2.2 ± 1.1[c]
4-nitro	4.6[b]		5.3 ± 0.2[e]		1.4 ± 0.1[e]
pentafluoro	2.7[f]	0.025 ± 0.002	0.029 ± 0.006[c]	0.005 ± 0.001	0.013 ± 0.006
Brønsted-type equation[g]		$-3.94 + 0.87\text{p}K_a$	$-1.41 + 1.00\text{p}K_a$	$-4.79 + 0.94\text{p}K_a$	$-1.32 + 0.91\text{p}K_a$

[a] The k_N values were measured in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M (KCl). [b] Values of pK_a taken from ref 8a, measured in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M. [c] Values obtained from eq 3. The values of k_H obtained from this equation for the reactions of TNPC are $(2 \pm 1) \times 10^8$ s^{-1} M^{-2} (4-methoxybenzenethiolate) and $(8 \pm 2) \times 10^3$ s^{-1} M^{-2} (pentafluorobenzenethiolate), respectively, and for the reactions of TNPTC are $(1.1 \pm 0.5) \times 10^8$ s^{-1} M^{-2} (benzenethiolate), $(6 \pm 3) \times 10^7$ s^{-1} M^{-2} (4-chlorobenzenethiolate), and $(2 \pm 1) \times 10^7$ s^{-1} M^{-2} (3-chlorobenzenethiolate). [d] Value of pK_a determined by interpolation of the linear relationship between the pK_a values measured in aqueous solution at 25.0 °C and an ionic strength of 0.2 M (ref 8a) and the thermodynamic pK_a values in water at 25.0 °C (ref 8b). [e] Values of k_N measured under second-order conditions (see text). [f] Value of pK_a measured in aqueous solution at 25.0 °C and an ionic strength of 1.0 M (ref 8c). [g] log k_N as a function of pK_a.

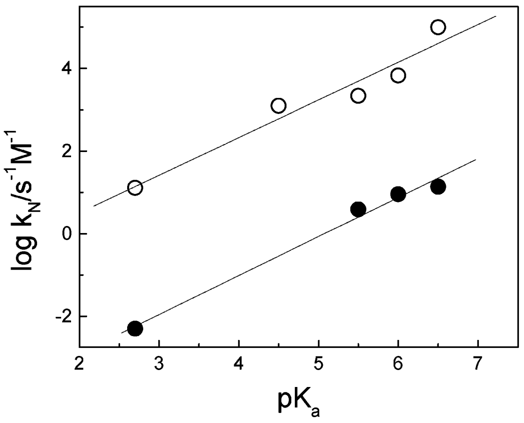

FIGURE 2. Brønsted-type plots obtained in the benzenethiolysis of *S*-(2,4-dinitrophenyl) ethyl thiolcarbonate (DNPTC, ●) and *S*-(2,4,6-trinitrophenyl) ethyl thiolcarbonate (TNPTC, ○), in aqueous solution, 25.0 °C, ionic strength 0.2 M. The slopes are $\beta = 0.9$.

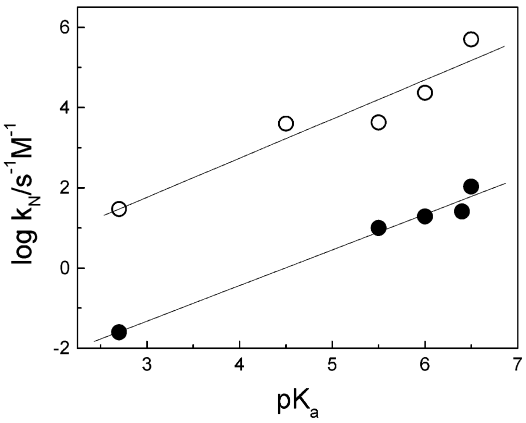

FIGURE 3. Brønsted-type plots obtained in the benzenethiolysis of 2,4-dinitrophenyl methyl carbonate (DNPC, ●) and 2,4,6-trinitrophenyl methyl carbonate (TNPC, ○), in aqueous solution, 25.0 °C, ionic strength 0.2 M. The slopes are $\beta = 0.9$ and 1.0, respectively.

shown in Figure 2. The plots are linear and have the same slope ($\beta = 0.9$) within the error limits.

The magnitudes of these Brønsted slopes are consistent with those found in the stepwise pyridinolysis of the same thiolcarbonates when decomposition to products of a zwitterionic tetrahedral intermediate ($T^{\pm}$) is rate limiting.[10] The slope values are also in accord with those obtained in the aminolysis of aryl acetates,[11a] diaryl carbonates,[11b] and acetyl chloride,[12] when breakdown of the intermediate $T^{\pm}$ to products is the rate-determining step. Therefore, it would seem that the benzenethiolysis of DNPTC and TNPTC would proceed through a tetrahedral intermediate (anionic in these cases), with its path to products being rate limiting. Nevertheless, if the mechanism were stepwise, the Brønsted-type plot for DNPTC would be biphasic, with a value of pK_a at the curvature center (p$K_a{}^0$) of 3.4, corresponding to pK_a value of 2,4-dinitrobenzenethiol.[13] This is the pK_a at which the hypothetical anionic tetrahedral intermediate (T^-) would break to reactants and products with equal rates.[14] The absence of this curvature within the pK_a range of the nucleophiles employed is a conclusive proof that the mechanism of these reactions is concerted.[14] The hypothetical intermediate T^- in the reaction of DNPTC could be so unstable that either it does not exist (enforced concerted mechanism) or its high energy skews the energy surface of the reaction to favor the concerted mechanism.[15] If the hypothetical intermediate T^- in the reaction of DNPTC were so unstable, T^- for the TNPTC benzenethiolysis would be even more unstable in view of the better nucleofuge involved (2,4,6-trinitrobenzenethiolate) compared with 2,4-dinitrobenzenethiolate ion. Therefore, if the benzenethiolysis of DNPTC were concerted it is more likely that the same reaction of TNPTC would also be concerted.

The Brønsted-type plots for the benzenethiolysis of DNPC and TNPC, obtained with the k_N values and the pK_a of the benzenethiols (Table 5), are shown in Figure 3. The plots are linear with slopes of 0.9 for DNPC and 1.0 for TNPC.

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(11) (a) Satterthwait, A. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7018. (b) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6963, 6970.

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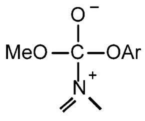
The magnitudes of these Brønsted slopes are consistent with those found in the stepwise pyridinolysis of the same carbonates when the decomposition to products of a tetrahedral intermediate (**1**) is rate limiting.[6b,c] The values of β are also in accord with those obtained in the stepwise aminolysis of similar acetates, carbonates, and their thiol derivatives when breakdown of the zwitterionic tetrahedral intermediate to products is rate determining.[9−13] Nevertheless, the similar values of β seem fortuitous, and we believe the reactions of benzenethiolates with DNPC and TNPC are not stepwise (through the tetrahedral intermediate **2**) but concerted, as will now be shown. The existence of a very similar intermediate (**3**) was ruled out in the phenolysis of *S*-aryl ethyl thiolcarbonates.[4a] This reaction is the microscopic reverse of the reaction under the present investigation and therefore must have the same mechanism. It is known that the change of methoxy to ethoxy in a similar intermediate does not alter significantly the rate constants for its decomposition nor its thermodynamic stability.[16] Therefore, it is reasonable that intermediate **2** is either too unstable to exist or very unstable. In either case the mechanism of the reactions of benzenethiolates with DNPC and TNPC would be concerted.



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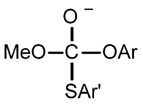

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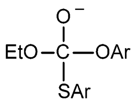
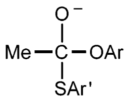


3

Another reason to believe that the benzenethiolysis of DNPC is concerted is that there is no Brønsted break for this reaction (Figure 3) near the pK_a of 2,4-dinitrophenol (pK_a 4.1 under the experimental conditions). If these reactions were stepwise there would be a break in the Brønsted plot at a pK_a value (pK_a^0) for which the rate constant for Ar′S$^-$ expulsion (k_{-1}) from the intermediate **2** (OAr = 2,4-dinitrophenoxy, DNPO) equals that for DNPO$^-$ expulsion (k_2). Although it is known that ArO$^-$ is a better nucleofuge compared to an *isobasic* Ar′S$^-$, as judged by elimination rate constants from the conjugate bases of the corresponding esters (E1cB mechanism),[17] presumably the rate constant k_2 (DNPO$^-$ expulsion from **2**) is not greater than k_{-1} (*isobasic* Ar′S$^-$ expulsion from **2**). 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 of 4-nitrophenol (NPOH) and DNPOH.[1a] Similarly, for the stepwise thiolysis of 4-nitrophenyl formate and pivalate the Brønsted pK_a^0 is ca. 7.[1b] The similar values of k_2 and k_{-1} for sulfur and oxygen *isobasic* groups has been attributed to the fact that both groups are attached to the same compound (e.g., intermediate **2**) and the larger leaving ability of ArO than an isobasic Ar′S is compensated by a smaller push by Ar′S compared to that by the isobasic ArO.[1a] Therefore, if the benzenethiolysis of DNPC were stepwise the pK_a^0 value would be ca. 4. The lack of a Brønsted break for the DNPC reactions, covering a pK_a range 2.7−6.5, indicates that this mechanism is not stepwise, confirming therefore the concerted process. The thiolysis of TNPC should also be concerted in view of the even more unstable "intermediate" that would be formed. These results augment those on the phenolysis of thiolcarbonates due to the microscopic reversibility.

The instability of the putative anionic tetrahedral intermediate **2** should be extremely high taking into account the groups attached to its central carbon. For the phenolysis of aryl acetates, Williams and co-workers have argued that two *O*-aryl groups are sufficient to destabilize an anionic tetrahedral intermediate to the point of nonexistence.[3a]

The fact that the tetrahedral intermediate **4** (Ar = NP or DNP), formed in the thiolysis of 4-nitrophenyl and 2,4-dinitrophenyl acetates,[1a] is more stable than the putative one (**2** Ar = NP or DNP) in the phenolysis of *S*-(4-nitrophenyl) ethyl thiolcarbonate[4a] and the thiolysis of 2,4-dinitrophenyl methyl carbonate (this work) indicates that the change of Me to MeO or EtO destabilizes intermediate **4**. A similar destabilization has been found in the aminolysis of thiolacetates and thiolcarbonates. The aminolyses (secondary alicyclic amines) of 2,4-dinitrophenyl and 2,4,6-trinitrophenyl thiolacetates are stepwise,[13] through intermediate **5** (Ar = DNP or TNP), whereas the same aminolyses of *S*-(2,4-dinitrophenyl) and *S*-(2,4,6-trinitrophenyl) ethyl thiolcarbonates are concerted.[7] The latter result indicates that intermediate **6** (Ar = DNP or TNP) is either too labile to qualify as an intermediate (enforced concerted mechanism) or it exists but it is so unstable that the concerted process is favored.[15]



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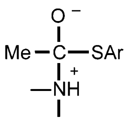

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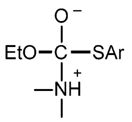

6

The greater reactivity of TNPC than DNPC and of TNPTC than DNPTC toward benzenethiolates (Table 5 and Figures 2 and 3) can be explained by the presence of a third nitro group in the trinitro substrates, which would destabilize the ground state of these compounds compared to those of the dinitro derivatives.[18] This would make the former compounds more prone to nucleophilic attack.[18] Furthermore, the trinitro nucleofuges should be expelled faster from these substrates than the more basic dinitro leaving groups from DNPC and DNPTC, respectively.

Figure 4 shows a comparison of the Brønsted plots for the nucleophilic rate constants for the benzenethiolysis (this work) and phenolysis[4b] of DNPC and TNPC, and Figure 5 shows a comparison of the same reactions[4a] of DNPTC and TNPTC. It can be seen that in all cases benzenethiolysis is faster than phenolysis toward a carbonyl carbon within the pK_a range studied. A similar result was found in the reactions of 4-nitrophenyl acetate[1a] and 4-nitrophenyl formate:[1b] benzenethiolates are more

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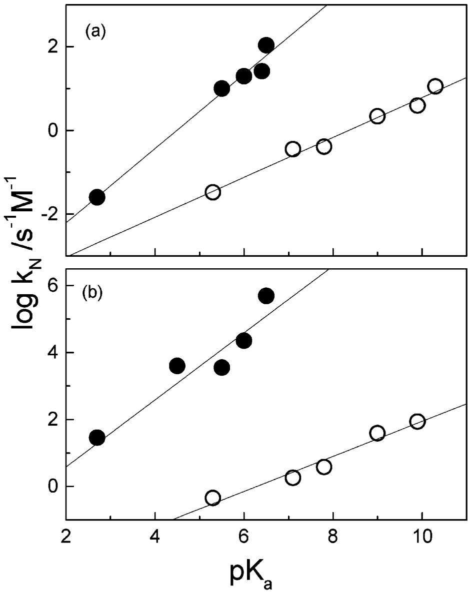

FIGURE 4. Brønsted-type plots obtained in the benzenethiolysis (●, this work) and phenolysis (○, ref 4b) of (a) 2,4-dinitrophenyl methyl carbonate (DNPC) and (b) 2,4,6-trinitrophenyl methy carbonate (TNPC), in aqueous solution, 25.0 °C, ionic strength 0.2 M.

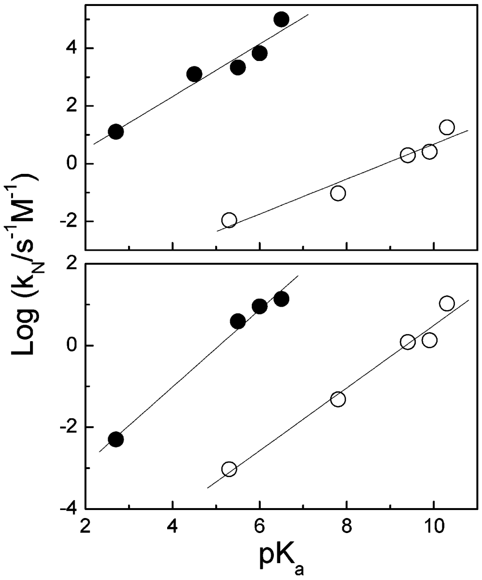

FIGURE 5. Brønsted-type plots obtained in the benzenethiolysis (●, this work) and phenolysis (○, ref 4a) of (a) 2,4-dinitrophenyl ethyl thiolcarbonate (DNPTC) and (b) 2,4,6-trinitrophenyl ethyl thiolcarbonate (TNPTC), in aqueous solution, 25.0 °C, ionic strength 0.2 M.

reactive toward these substrates than *isobasic* phenoxide anions. This was attributed to the softer nature of the sulfur nucleophile, relative to the oxygen nucleophile,[19] that would prefer to bind to the relatively soft carbonyl carbon. This can be confirmed by the fact that benzenenethiolates show an additional rate enhancement, relative to isobasic phenoxide ions, toward 4-nitrophenyl thiolacetate, which possesses a softer electrophilic group than that of the corresponding carbonate.[1a]

The Brønsted slopes found for the concerted phenolyses of DNPC, TNPC, DNPTC, and TNPTC are 0.48, 0.52, 0.77, and 0.61, respectively.[4a,b] These slopes are smaller than those obtained in the concerted benzenethiolysis of these compounds (this work): $\beta = 0.9$ for DNPC, DNPTC, and TNPTC and $\beta = 1.0$ for TNPC. This means that the bond formation between the sulfur nucleophiles and the carbonyl carbon is more advanced in the transition state, relative to reactants, than that between the oxygen nucleophiles and the same carbon atom. The larger Brønsted slopes for the faster reactions of benzenethiolates is against the reactivity-selectivity principle and the Hammond postulate.[20] Nevertheless, there are many concerted reactions which do not follow the reactivity-selectivity principle. For instance, in the concerted (S_N2) reactions of anilines with benzyl bromides and benzoyl chlorides in acetonitrile, the magnitude of the Hammett ρ_{nuc} constant increases with the increasing reactivity of the substrates.[21] Also in the concerted phenolyses of aryl acetates the transition state is tighter for the more basic nucleophiles.[22] Shaik has also found that S_N2 (concerted) reactions usually break the reactivity-selectivity and Bell−Evans−Polanyi principles.[23] Similar findings have been reported by Lee[24] and Williams.[25]

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