

Kinetic Study of the Phenolysis of Bis(4-nitrophenyl) Carbonate, Bis(4-nitrophenyl) Thionocarbonate, and Methyl 4-Nitrophenyl Thionocarbonate

Enrique A. Castro,* Mauricio Angel, David Arellano, and José G. Santos*

Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile

ecastro@puc.cl.

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The reactions of a homogeneous series of phenols with bis(4-nitrophenyl) carbonate (BNPC), bis(4-nitrophenyl) thionocarbonate (BNPTOC), and methyl 4-nitrophenyl thionocarbonate (MNPTOC) are subjected to a kinetic investigation in water, at 25.0 °C and ionic strength of 0.2 M (KCl). Under excess of phenol over the substrate, all the reactions obey pseudo-first-order kinetics and are first order in phenoxide anion. The reactions of BNPC show a linear Brønsted-type plot with slope $\beta = 0.66$, consistent with a concerted mechanism (one step). In contrast, those of BNPTOC and MNPTOC show biphasic Brønsted-type plots with slopes $\beta = 0.30$ and 0.44 , respectively, at high pK_a , and $\beta = 1.25$ and 1.60 , respectively, at low pK_a , consistent with stepwise mechanisms. For the reactions of both thionocarbonates, the pK_a value at the center of the Brønsted plot (pK_a^0) is 7.1, which corresponds to the pK_a of 4-nitrophenol. This confirms that the phenolyses of the thionocarbonates are stepwise processes, with the formation of an anionic tetrahedral intermediate. By the comparison of the kinetics and mechanisms of the title reactions with similar reactions, the following conclusions can be drawn: (i) Substitution of S^- by O^- in an anionic tetrahedral intermediate (T^-) destabilizes it. (ii) The change of MeO by 4-nitrophenoxy in T^- results in an increase of both the rate constant and equilibrium constant, for the formation of T^- , and also in an enlargement of the rate coefficient for the expulsion of 4-nitrophenoxide from T^- . (iii) Substitution of an amino group in a tetrahedral intermediate by ArO destabilizes it. (iv) Secondary alicyclic amines and other amines show greater reactivity toward MNPTOC than isobasic phenoxide anions.

Introduction

Although the kinetics and mechanisms of the phenolyses of esters are well documented,^{1,2} only few reports have dealt with the kinetics of the same reactions of carbonates and thiocarbonates.³ Among the latter reactions are the phenolyses of 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl *O*-ethyl thiolcarbonates^{3a} and 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl methyl carbonates.^{3b} All these reactions have been found to be governed by concerted mechanisms, on the basis of the linear Brønsted-type plots obtained and the magnitude of their slopes.³ Moreover, for the phenolysis of 4-nitrophenyl methyl carbonate the concerted mechanism was confirmed by the fact that the predicted Brønsted break for a stepwise mechanism (at $pK_a = 7.1$) was not observed within the pK_a of the phenols used.^{3b}

To extend our kinetic studies on the phenolyses of carbonates and thiocarbonates, in this work, we investigate the kinetics and mechanisms of the phenolyses of bis(4-nitrophenyl) carbonate (BNPC) and two thionocarbonates: bis(4-nitrophenyl) thionocarbonate (BNPTOC) and methyl 4-nitrophenyl thionocarbonate (MNPTOC).

Another aim is to assess the influence of the electrophilic (CO vs CS) and nonleaving groups and the nature of the nucleophile on the kinetics and mechanism of these reactions. This objective will be achieved by the comparison of the reactions of the present work with the phenolysis of 4-nitrophenyl methyl carbonate^{3b} and the aminolysis of BNPTOC⁴ and MNPTOC.⁵



Experimental Section

Materials. The phenols were purified by distillation or recrystallization. BNPC was purchased from Aldrich. BNPTOC^{4,6} and MNPTOC⁷ were synthesized as reported. Bis(phenyl) carbonate (one of the products in the reaction of

* To whom correspondence should be addressed.

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Table 1. Experimental Conditions and k_{obsd} Values for the Phenolysis of Bis(4-nitrophenyl) Carbonate (BNPC)^a

phenoxide substituent	pH	F_N^b	$10^3[\text{ArOH}]_{\text{tot}}$ (M) ^c	10^2k_{obsd} (s ⁻¹)	no. of runs
4-OCH ₃	8.7 ^d	0.025	0.50–3.0	0.520–1.65	5
	9.0 ^d	0.048	0.50–3.0	0.680–2.53	5
	9.3 ^d	0.090	0.50–3.0	1.41–4.27	5
H	9.0	0.112	0.5–3.0	0.19–1.70	6
	9.3	0.200	0.5–3.0	0.44–3.06	6
	9.6	0.285	0.5–3.0	1.22–3.76	6
3-Cl	8.7	0.333	0.5–3.0	0.58–2.39	6
	9.0	0.500	0.5–3.0	0.95–3.30	6
	9.3	0.667	0.5–3.0	1.27–4.07	6
4-CN	7.5	0.333	10.0–60.0	1.87–8.26	6
	7.8	0.500	10.0–60.0	2.60–15.6	6
	8.1	0.667	10.0–60.0	2.62–18.7	6
2,6-F ₂	8.7 ^d	0.974	2.0–10.0	0.58–2.06	5
	9.0 ^d	0.987	2.0–10.0	0.76–2.18	5
	9.3 ^d	0.993	2.0–10.0	0.80–2.19	5
2,3,4,5,6-F ₅	6.7 ^e	0.962	30.0–70.0	0.203–0.347	5
	7.0 ^e	0.980	30.0–70.0	0.188–0.382	5
	7.3 ^e	0.990	30.0–70.0	0.206–0.387	5

^a In aqueous solution, at 25.0 °C, and ionic strength of 0.2 M (KCl). ^b Fraction of free phenoxide. ^c Concentration of total phenol (free phenoxide plus conjugate acid). ^d In the presence of borate buffer (0.005 M). ^e In the presence of phosphate buffer (0.005 M).

phenol with BNPC) was obtained from Aldrich. Phenyl 4-nitrophenyl carbonate (another product of the latter reaction) was prepared by a modification⁸ of a procedure reported.⁹ Phenyl 4-nitrophenyl thionocarbonate (one of the products of the reaction of phenol with BNPTOC) was obtained in poor yield by the method described;⁶ a better yield was found by another procedure.⁵ Bis(phenyl) thionocarbonate (another product of the latter reaction) was synthesized as reported.⁴ Methyl phenyl thionocarbonate (one of the products of the reaction of phenol with MNPTOC) was prepared by the same method used for the synthesis of MNPTOC.⁷

Kinetic Measurements. These were performed spectrophotometrically by following the production of 4-nitrophenoxide ion at 400 nm, by means of a Hewlett-Packard 8453 diode array spectrophotometer. The reactions were studied in aqueous solutions, at 25.0 ± 0.1 °C, ionic strength of 0.2 M (maintained with KCl), and at least a 10-fold excess of total phenol (phenoxide plus phenol) over the substrate.

Pseudo-first-order rate coefficients (k_{obsd}) were found through-out, mostly by means of the “infinity” method; for the slowest reactions (BNPTOC and MNPTOC with pentafluorophenol), the initial rate method was used.¹⁰

In the reactions of the symmetrical substrates (BNPC and BNPTOC) with phenoxides, a slow reaction of these nucleophiles with the initial product (phenyl 4-nitrophenyl carbonate and the analogous thionocarbonate, respectively) was noticed. This reaction was much slower than the major one and, therefore, did not interfere with the main reaction, as indicated by the good correlation coefficients obtained.

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

Product Studies. In all the reactions the 4-nitrophenoxide ion was identified as one of the products by the comparison of the UV–vis spectra, after completion of these reactions, with those of authentic samples of 4-nitrophenol under the same reaction conditions.

In the reactions of BNPC and BNPTOC with unsubstituted phenoxide anions, phenyl 4-nitrophenyl carbonate and phenyl 4-nitrophenyl thionocarbonate, respectively, were found as the other products of these reactions. After the kinetics were measured, a slow reaction of phenoxide with these products was observed, yielding bis(phenyl) carbonate and bis(phenyl) thionocarbonate, respectively. All these products were identi-

Table 2. Experimental Conditions and k_{obsd} Values for the Phenolysis of Bis(4-nitrophenyl) Thionocarbonate (BNPTOC)^a

phenoxide substituent	pH	F_N^b	$10^3[\text{ArOH}]_{\text{tot}}$ (M) ^c	10^2k_{obsd} (s ⁻¹)	no. of runs
4-OCH ₃	10.0	0.333	3.0–10.0	3.58–9.45	5
	10.3	0.500	3.0–10.0	5.49–14.0	5
	10.6	0.667	3.0–10.0	7.12–18.2	5
H	9.6	0.333	3.0–10.0	2.25–7.26	5
	9.9	0.500	3.0–10.0	3.97–10.8	5
	10.2	0.667	3.0–10.0	5.08–14.1	5
4-Cl	9.1	0.333	3.0–10.0	2.31–5.11	5
	9.4	0.500	3.0–10.0	3.00–7.65	5
	9.7	0.667	3.0–10.0	3.53–10.1	5
3-Cl	8.7	0.333	0.50–3.00	0.57–1.36	6
	9.0	0.500	0.50–3.00	0.66–2.16	6
	9.3	0.667	0.50–3.00	0.81–2.62	4
4-CN	7.5	0.333	40.0–80.0	5.15–10.6	5
	7.8	0.500	40.0–80.0	6.54–15.8	5
	8.1	0.667	40.0–80.0	8.63–19.7	5
2,6-F ₂	8.7 ^d	0.974	4.0–12.0	1.23–2.44	5
	9.0 ^d	0.987	4.0–12.0	1.29–2.53	5
	9.3 ^d	0.993	4.0–12.0	1.52–2.50	5
2,3,4,5,6-F ₅	8.0 ^e	0.998	100–500	0.396–0.998	5

^a In aqueous solution, at 25.0 °C, and ionic strength of 0.2 M (KCl). ^b Fraction of free phenoxide. ^c Concentration of total phenol (free phenoxide plus conjugate acid). ^d In the presence of borate buffer (0.005 M). ^e In the presence of phosphate buffer (0.005 M).

Table 3. Experimental Conditions and k_{obsd} Values for the Phenolysis of Methyl 4-Nitrophenyl Thionocarbonate (MNPTOC)^a

phenoxide substituent	pH	F_N^b	$10^3[\text{ArOH}]_{\text{tot}}$ (M) ^c	10^2k_{obsd} (s ⁻¹)	no. of runs
4-OCH ₃	10.0	0.333	0.6–8.0	4.0–42.5	6
	10.3	0.500	1.0–8.0	8.7–60.4	5
	10.6	0.667	1.0–8.0	11.2–72.3	5
H	9.4	0.258	0.6–6.0	0.89–7.23	5
	9.7	0.409	0.6–6.0	1.31–12.9	5
	10.0	0.580	0.6–6.0	1.87–15.8	5
3-Cl	8.7	0.333	0.6–6.0	0.79–5.90	5
	9.0	0.500	0.6–6.0	1.04–9.06	5
	9.3	0.667	0.6–6.0	1.32–11.1	5
4-CN	7.5	0.333	1.0–9.0	0.26–1.77	5
	7.8	0.500	1.0–9.0	0.43–2.86	5
	8.1	0.667	1.0–9.0	0.54–3.91	5
2,6-F ₂	7.1	0.483	1.0–9.0	0.102–0.818	5
	7.4	0.651	1.0–9.0	0.127–1.07	5
	7.8	0.824	1.0–8.0	0.194–1.28	5
2,3,4,5,6-F ₅	7.2 ^d	0.988	10.0–50.0	0.0134–0.0296	4

^a In aqueous solution, at 25.0 °C, and ionic strength of 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).

fied by HPLC, using as standards the authentic samples. HPLC conditions were as follows: column, Eurospher C-18 (10 cm, 7 μm); eluant, acetonitrile/water = 70:30; isocratic mode, 0.7 mL/min.

In the reactions of MNPTOC with unsubstituted phenoxide, the presence of methyl phenyl thionocarbonate in the reaction media was determined by HPLC, using the latter product as reference. The HPLC conditions were as described above.

Results and Discussion

The rate law obtained in all the reactions under investigation is given by eqs 1 and 2, where NP is 4-nitrophenyl, S and ArO⁻ represent a substrate and a substituted phenoxide nucleophile, and k_0 and k_N are the hydrolysis and nucleophilic rate constants, respectively.

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

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

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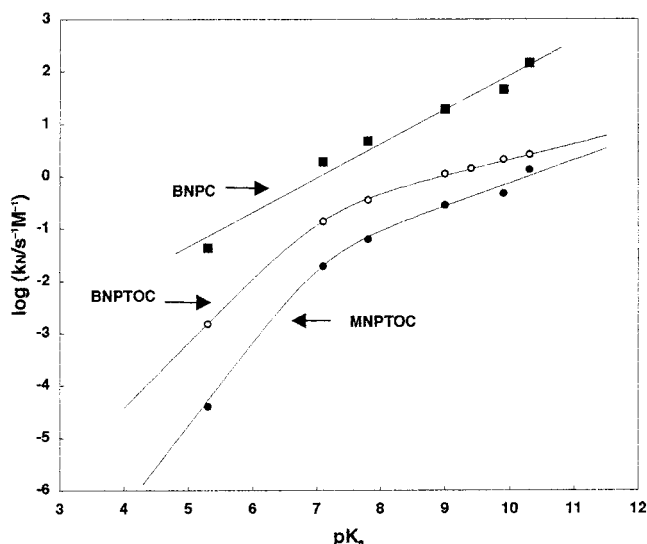
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Table 4. Values of pK_a of Phenols and k_N for the Phenolysis of Bis(4-nitrophenyl) Carbonate (BNPC), Bis(4-nitrophenyl) Thionocarbonate (BNPTOC), and Methyl 4-Nitrophenyl Thionocarbonate (MNPTOC)^a

phenoxide substituent	pK_a	k_N ($s^{-1} M^{-1}$)		
		BNPC	BNPTOC	MNPTOC
4-OCH ₃	10.3	144 ± 6	2.6 ± 0.1	1.35 ± 0.04
H	9.9	45 ± 3	2.1 ± 0.1	0.47 ± 0.02
4-Cl	9.4		1.4 ± 0.1	
3-Cl	9.0	19 ± 1	1.10 ± 0.05	0.28 ± 0.01
4-CN	7.8	4.7 ± 0.2	0.35 ± 0.02	0.062 ± 0.004
2,6-F ₂	7.1	1.9 ± 0.1	0.136 ± 0.007	0.019 ± 0.001
2,3,4,5,6-F ₅	5.3	0.043 ± 0.002	0.0015 ± 0.0001	0.00004 ± 0.00001

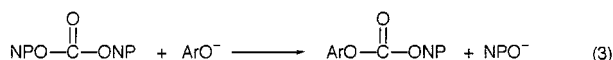
^a Both the pK_a and k_N values were determined in aqueous solution, at 25.0 °C, and ionic strength of 0.2 M (KCl).

**Figure 1.** Brønsted-type plots for the phenolyses of bis(4-nitrophenyl) carbonate (BNPC), bis(4-nitrophenyl) thionocarbonate (BNPTOC), and methyl 4-nitrophenyl thionocarbonate (MNPTOC) in aqueous solution, at 25.0 °C with ionic strength of 0.2 M (KCl).

The value of k_0 was much lower than the second term (phenolysis) of eq 2, except in the slow reactions of pentafluorophenol with the three substrates, where the phenolysis term was also small. The k_N values were obtained as the slopes of linear plots of k_{obsd} vs $[ArO^-]$. These values were found to be independent of pH. The k_N values determined for the phenolyses of the three substrates, together with the pK_a values of the different phenols employed, are shown in Table 4.

With the use of the k_N and pK_a values of Table 4 (measured under the same experimental conditions) the three Brønsted-type plots of Figure 1 were obtained.

The Brønsted-type plot for the phenolysis of BNPC is linear with slope $\beta = 0.66$ (Figure 1), which is consistent with a concerted mechanism (eq 3, NP = 4-nitrophenyl) with no intermediate. Similar β values have been found in the concerted phenolyses of 2,4-dinitrophenyl and 2,4,6-trinitrophenyl *O*-ethyl thiolcarbonates ($\beta = 0.77$ and 0.61, respectively),^{3a} 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl methyl carbonates ($\beta = 0.67$, 0.48, and 0.52, respectively),^{3b} aryl acetates ($\beta = 0.53$ –0.66),^{1c,d,2} and acetic anhydride ($\beta = 0.58$).^{1d}

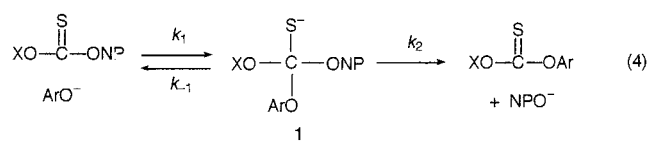


The best proof that the phenolysis of BNPC is concerted is the fact that there is no break at $pK_a = 7.1$ (the

pK_a of 4-nitrophenol) in the Brønsted-type plot of Figure 1.¹¹ If this reaction were stepwise, with the formation of an anionic tetrahedral intermediate (T^-), the rate constants for the decomposition of T^- to reactants and products would be equal at $pK_a = 7.1$.^{8,11} Therefore, for nucleophiles (phenoxides) that are less basic than 4-nitrophenoxide, the breakdown of T^- to products would be rate determining, and for those nucleophiles that are more basic than 4-nitrophenoxide, formation of T^- would be the rate-limiting step. Therefore, for a stepwise mechanism a biphasic Brønsted plot is expected, with linear relationships over the rate-determining step regions and a curvature (break) between that is centered at the pK_a of the leaving group.⁸ The lack of such curvature at $pK_a = 7.1$ rules out the stepwise mechanism for the phenolysis of BNPC.

A referee has pointed out that the phenolysis of BNPC could be stepwise in view of the fact that in the Brønsted plot the pentafluorophenol point falls off the straight line through the other points. Nevertheless, we think this falloff is too small to qualify for a stepwise mechanism. A similar slight falloff for pentafluorophenol has been found in the concerted phenolysis of 4-nitrophenyl acetate.² However, the stepwise mechanism for the phenolysis of BNPC cannot be rigorously excluded.

The Brønsted-type plots for the phenolysis of the two thionocarbonates, BNPTOC and MNPTOC, are biphasic (see Figure 1), with slopes $\beta_1 = 0.30$ and 0.44, respectively, at high pK_a , and $\beta_2 = 1.25$ and 1.60, respectively, at low pK_a . Both plots have breaks at $pK_a = 7.1$ (pK_a of 4-nitrophenol), which is consistent with the occurrence of stepwise mechanisms (eq 4, X = methyl or 4-nitrophenyl), as discussed above.

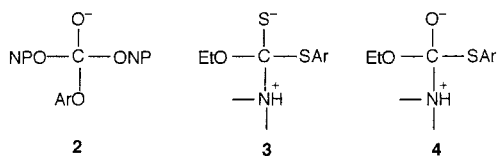


According to our results, the tetrahedral intermediate **1**, although unstable, does exist. In contrast, the tetrahedral species **2** is either more unstable than **1** or nonexistent. In the former case, the reaction chooses the path of lower free energy, which is the concerted mechanism. If **2** does not exist, the concerted process is enforced, i.e., this mechanism takes place because the stepwise route is impossible.¹²

In accordance to our findings, the phenolysis of methyl 4-nitrophenyl carbonate is concerted,^{3b} whereas the reac-

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tion of the same nucleophiles with MNPTOC is stepwise (this work). This means that the substitution of S^- in intermediate **1** ($X = Me$) by O^- destabilizes the intermediate in such a way as to change the mechanism.

The destabilization of a tetrahedral intermediate by the substitution of S^- by O^- has precedents in the aminolysis of compounds similar to the title substrates. The reactions of secondary alicyclic amines with 2,4-dinitrophenyl and 2,4,6-trinitrophenyl *O*-ethyl thiolcarbonates have been found to be concerted.¹³ In contrast, the reactions of the same amines with 2,4-dinitrophenyl and 2,4,6-trinitrophenyl *O*-ethyl dithiocarbonates are governed by stepwise mechanisms.¹⁴ This means that the zwitterionic tetrahedral intermediate **3** is less unstable than **4**; i.e., species **3** is destabilized by the change of S^- to O^- .

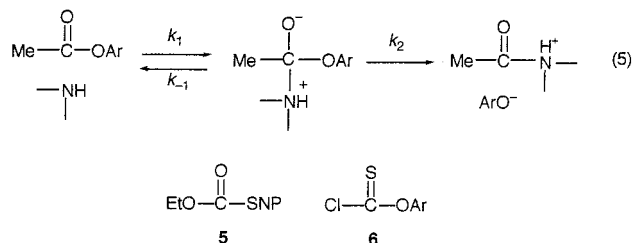
This has been attributed to the greater ability of O^- in a tetrahedral intermediate to form a double bond and expel a nucleofuge, when compared to S^- , due to a stronger π -bonding energy of the carbonyl group relative to thiocarbonyl.¹⁵ In agreement with this, it has been found that expulsions of PhS^- and an amine from the zwitterionic tetrahedral intermediate formed in the aminolysis of phenyl thiolacetate (similar to **4**, Me in place of EtO) are much faster than those from the tetrahedral species formed in the same aminolysis of phenyl dithioacetate (similar to **3**).¹⁶

According to Figure 1, BNPTOC has a larger value of k_N than MNPTOC, irrespective of which step is rate determining. The larger reactivity of BNPTOC than MNPTOC toward phenoxides, when the k_1 step of eq 4 is rate limiting, can be ascribed to the strong electron withdrawal from intermediate **1** by NPO relative to the electron-releasing effect of MeO. When the k_2 step of eq 4 is rate determining, $k_N = K_1k_2$, where K_1 is the equilibrium constant for the first step. In this case, the larger k_N values for the reactions of BNPTOC than those for MNPTOC can be attributed to larger values of both K_1 and k_2 for the former reactions. The larger K_1 value can be explained by the same argument given above for k_1 . The larger value of k_2 for BNPTOC can be ascribed to two factors: (i) The tetrahedral intermediate formed in the BNPTOC reactions (**1**, $X = NP$) possesses two NPO leaving groups, which gives it a statistical advantage (factor of 2) over the NPO leaving from the other intermediate (**1**, $X = Me$). (ii) The intermediate **1** ($X = NP$) has its central carbon atom more positively charged (due to its two NPO groups) than that of **1** ($X = Me$), thereby facilitating the formation of the CS double bond and the expulsion of the leaving group from the former intermediate.

The concerted phenolysis of BNPC (this work) is much faster than the concerted reactions of the same nucleophiles with methyl 4-nitrophenyl carbonate^{3b} (e.g., unsubstituted phenoxide reacts 60 times faster with the former substrate). This means that the change of NP to Me in BNPC decreases the value of k_N . This can be ascribed to the stronger electron-withdrawing effect of NPO compared to MeO, as discussed above.

The reactions of secondary alicyclic (SA) amines with BNPTOC exhibit a nonlinear Brønsted-type plot with slopes $\beta = 0.1$ and 0.5 at high and low pK_a , respectively. The slight Brønsted curvature was attributed to a concerted mechanism, although the stepwise process was not rigorously ruled out.⁴ In light of our result that the phenolysis of this substrate is stepwise, it seems more likely that the above aminolysis is stepwise, for the following reasons.

The reactions of SA amines with 4-nitrophenyl and 2,4-dinitrophenyl acetates^{17,18} are stepwise (eq 5) whereas the phenolyses of these compounds are concerted.^{1d,2} Other examples are the stepwise aminolyses (SA amines) of 4-nitrophenyl *O*-ethyl thiolcarbonate (**5**)¹⁹ and phenyl and 4-nitrophenyl chlorothionoformates (**6**),²⁰ compared to the concerted phenolyses of the same substrates.^{3a,21} All these examples indicate that the change of an amino group, in a zwitterionic tetrahedral intermediate, to ArO destabilizes the intermediate.



For the pyridinolysis of MNPTOC, a linear Brønsted-type plot of slope 1.0 was found.⁷ This was explained by a stepwise mechanism where the breakdown to products of the zwitterionic tetrahedral intermediate ($T^\pm$) is the rate-determining step.⁷ The lack of a Brønsted break for the pyridinolysis of this substrate (compared to the break at $pK_a = 7.1$ for its phenolysis) can be explained by the superior nucleofugality from $T^\pm$ of a pyridine relative to an isobasic aryl oxide from intermediate **1** ($X = Me$). This is evident from the fact that the Brønsted breaks found in the pyridinolyses of methyl 2,4-nitrophenyl carbonate,^{22a} 2,4-nitrophenyl acetate,^{22b} methyl 2,4,6-trinitrophenyl carbonate,²³ and 2,4,6-trinitrophenyl acetate²³ are at pK_a values that are much larger than those of the leaving groups.

In the reactions of SA amines with MNPTOC, nonlinear upward plots of k_{obsd} vs [amine] were found, which

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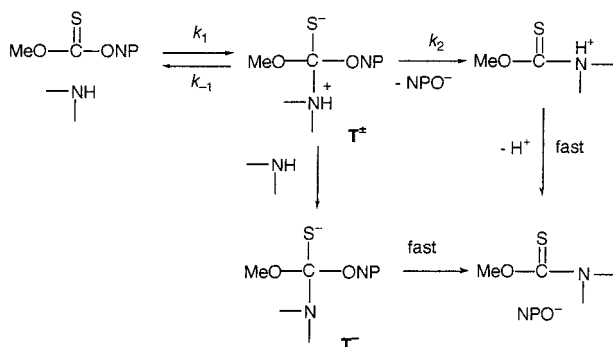
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Scheme 1



were interpreted by the formation of two tetrahedral intermediates of which one was zwitterionic ($T^\pm$, Scheme 1) and another was anionic (T^-).⁵ Base catalysis by the amine for the conversion of $T^\pm$ to T^- was claimed to be responsible for the upward curved plots of k_{obsd} vs

[amine]. From these plots, the values of the microscopic rate constants for the formation of $T^\pm$ (k_1) were obtained by fitting.⁵

The k_1 values for the aminolysis (SA amines) of MNPTOC are greater than those obtained in this work for the reactions of the same compound with isobasic phenoxides, when the first step of eq 4 is rate determining. Amines are also more reactive than isobasic phenoxides toward thiocarbonyl compounds when the breakdown of the tetrahedral intermediate to products is the rate-limiting step. Examples are the greater reactivities of pyridine ($pK_a = 5.37$)^{4,7} than pentafluorophenoxide ($pK_a = 5.3$, this work) toward MNPTOC and BNPTOC, which amount to 10-fold⁷ and 35-fold,⁴ respectively. The higher reactivity of carbonyl derivatives toward amines compared to isobasic aryloxides has been documented previously.^{17a,24}

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