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# Kinetics and Mechanisms of the Pyridinolysis of Phenyl and 4-Nitrophenyl Chlorothionoformates. Formation and Hydrolysis of 1-(Aryloxythiocarbonyl)pyridinium Cations

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The title reactions are subjected to a kinetic study in water, at 25.0 °C, and an ionic strength of 0.2 M (KCl). By following the reactions spectrophotometrically two consecutive reactions are observed: the first is formation of the corresponding thionocarbamates (1-(aryloxythiocarbonyl)-pyridinium cations) and the second is their decomposition to the corresponding phenol and pyridine, and COS. Pseudo-first-order rate coefficients ($k_{obsd1}$ and $k_{obsd2}$, respectively) are found under excess amine. Plots of $k_{obsd1}$ vs free pyridine concentration at constant pH are linear, with the slope ($k_N$) independent of pH. The Brønsted-type plots (log $k_N$ vs p$K_a$ of the conjugate acids of the pyridines) are linear with slopes $\beta = 0.07$ and 0.11 for the reactions of phenyl and 4-nitrophenyl chlorothionoformates, respectively. These Brønsted slopes are in agreement with those found in other stepwise reactions of the same pyridines in water, where the formation of a tetrahedral intermediate is the rate-determining step. In contrast to the stepwise mechanism of the title reactions that for the reactions of the same substrates with phenols is concerted, which means that substitution of a pyridino moiety in a tetrahedral intermediate by a phenoxy group destabilizes the intermediate. The second reaction corresponds to the pyridine-catalyzed hydrolysis of the corresponding 1-(aryloxythiocarbonyl)pyridinium cation. Plots of $k_{obsd2}$ vs free pyridine concentration at constant pH are linear, with the slope ($k_H$) independent of pH. The Brønsted plots for $k_H$ are linear with slopes $\beta = 0.19$ and 0.26 for the reactions of the phenyl and 4-nitrophenyl derivatives, respectively. These low values are explained by the fact that as p$K_a$ increases the effect of a better pyridine catalyst is compensated by a worse leaving pyridine from the corresponding thionocarbamate

## Introduction

Although much attention has been focused on the kinetics and mechanisms of the solvolysis[1] and aminolysis[2] of chloroformates, much less is known on the mechanisms of the solvolysis,[3] phenolysis,[4] and aminolysis[5] of chlorothionoformates.

The pyridinolysis of phenyl and 4-nitrophenyl chloroformates in acetonitrile exhibits linear Brønsted-type plots with slopes ($\beta$) of ca. 0.3, which were attributed to a stepwise mechanism where the formation of a zwitterionic tetrahedral intermediate ($T^{\pm}$) is the rate-determining step.[2d]

The solvolysis of phenyl chlorothionoformate (PClTF) in aqueous ethanol and aqueous acetone mixtures was found to be driven by an addition−elimination reaction at the trigonal carbon.[3a] In contrast, the solvolysis (methanol, ethanol, and their aqueous mixtures) of the same substrate was found to be subjected to a general-base-catalyzed $S_N2$ pathway.[3b]

The reactions of PClTF and 4-nitrophenyl chlorothionoformate (NPCITF) with substituted phenolates in water are governed by a concerted mechanism, as shown by the linear Brønsted-type plots obtained, with slopes ($\beta$) of 0.55 and 0.47, respectively.[4]

On the other hand, the aminolysis (secondary alicyclic amines) of PCITF and NPCITF in water exhibits linear Brønsted-type plots with the same slope, $\beta$ 0.26, consistent with a stepwise process, where the formation of the intermediate $T^{\pm}$ is rate limiting.[5]

In the present work, we undergo a kinetic and mechanistic study of the reactions of pyridines with the title

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**TABLE 1. Experimental Conditions and Values of $k_{obsd1}$ (fast process) and $k_{obsd2}$ (Slow Process) for the Pyridinolysis of PCITF[a]**

| pyridine substituent | pH | $10^3[N]_{tot}$ (M) | $10^3k_{obsd1}$ ($s^{-1}$) | $10^3k_{obsd2}$ ($s^{-1}$) | no. of runs |
|---|---|---|---|---|---|
| 4-$N(CH_3)_2$ | 6.50 | 1.0−10.0 | 0.11−0.27 | | 7 |
| | 6.80 | 0.70−10.0 | 0.96−3.96 | | 9 |
| | 7.10 | 0.70−7.0 | 1.35−5.21 | | 7 |
| 4-$NH_2$ | 6.50 | 9.0−90 | 2.90−25.8 | | 7 |
| | 6.80 | 1.0−50 | 2.11−24.3 | | 7 |
| | 7.10 | 5.0−50 | 6.36−58.7 | | 7 |
| 3.4-$(CH_3)_2$ | 6.50 | 0.15−1.05 | | 1.61−8.00 | 7 |
| | 6.80 | 0.15−0.90 | 29−101 | 1.69−9.90 | 6 |
| | 7.10 | 0.15−0.90 | 29.5−111 | 2.86−11.7 | 6 |
| 4-$CH_3$ | 6.50 | 0.40−3.40 | 46−370 | 6.90−35.9 | 6 |
| | 6.80 | 0.20−2.00 | 35.5−234 | 6.44−27.5 | 7 |
| | 7.10 | 0.40−4.00 | 40.1−319 | 7.65−30.3 | 6 |
| H | 5.00[b] | 0.15−1.00 | | 2.30−9.40 | 7 |
| | 6.50 | 0.20−1.10 | 27.3−156 | 4.71−17.3 | 7 |
| | 6.80 | 0.25−1.00 | 41.8−144 | | 6 |
| | 7.10 | 0.30−1.50 | 50.1−227 | | 6 |
| | 6.80 | 0.10−1.00 | | 4.17−15.4 | 7 |
| | 7.10 | 0.15−1.05 | | 4.60−18.1 | 6 |
| 3-$CONH_2$ | 3.40[b] | 0.20−0.32 | 16.0−23.0 | | 2 |
| | 5.00[c] | 0.30−1.20 | 37.4−118 | | 5 |
| | 6.50 | 0.20−1.10 | | 2.22−9.45 | 7 |
| | 6.80 | 0.15−1.00 | | 1.88−8.68 | 7 |
| | 7.10 | 0.25−0.90 | | 2.60−7.62 | 6 |
| 4-CN | 6.50 | 4.0−60.0 | | 16.4−129 | 7 |
| | 6.80 | 8.0−80.0 | | 17.4−176 | 7 |
| | 7.10 | 4.0−40.0 | | 8.45−81.2 | 7 |

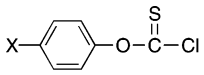
[a] In aqueous solution, at 25.0 °C, an ionic strength of 0.2 M, and under the presence of phosphate buffer 0.005 M, unless otherwise stated. [b] Without external buffer. [c] Under the presence of citrate buffer 0.005 M.

**TABLE 2. Experimental Conditions and Values of $k_{obsd1}$ (Fast Process) and $k_{obsd2}$ (Slow Process) for the Pyridinolysis of NPCITF[a]**

| pyridine substituent | pH | $10^3[N]_{tot}$ (M) | $10^3k_{obsd1}$ ($s^{-1}$) | $10^3k_{obsd2}$ ($s^{-1}$) | no. of runs |
|---|---|---|---|---|---|
| 4-$N(CH_3)_2$ | 6.50 | 1.0−10.0 | 2.44−4.95 | | 7 |
| | 6.80 | 1.0−10.0 | 3.49−8.27 | | 7 |
| | 7.10 | 0.70−7.0 | 3.10−10.1 | | 7 |
| 4-$NH_2$ | 6.50 | 9.0−90 | 6.90−61.0 | | 7 |
| | 6.80 | 5.5−50 | 7.55−62.4 | | 7 |
| | 7.10 | 5.0−50 | 17.4−133 | | 7 |
| 3.4-$(CH_3)_2$ | 6.50 | 0.15−0.90 | | 21.6−41.5 | 6 |
| | 6.80 | 0.15−0.90 | | 20.9−48.9 | 6 |
| | 7.10 | 0.15−0.75 | | 22.1−49.8 | 5 |
| 4-$CH_3$ | 6.50 | 0.40−3.40 | | 32.9−93.8 | 6 |
| | 6.80 | 0.20−2.20 | | 20.6−75.2 | 7 |
| | 7.10 | 0.40−4.00 | | 16.9−85.7 | 7 |
| H | 6.50 | 0.35−1.10 | | 12.2−35.0 | 6 |
| | 6.80 | 0.25−1.00 | | 11.8−35.5 | 6 |
| | 7.10 | 0.30−1.05 | | 16.2−40.2 | 6 |
| 3-$CONH_2$ | 3.40[b] | 0.20−0.32 | 44.2−53.0 | | 2 |
| | 5.00[c] | 0.30−1.20 | 62.3−169 | | 6 |
| | 6.50 | 0.20−1.10 | | 2.27−10.5 | 7 |
| | 6.80 | 0.15−1.00 | | 2.18−9.85 | 7 |
| | 7.10 | 0.25−0.90 | | 3.47−9.50 | 6 |
| 4-CN | 1.90[b] | 0.30−0.70 | 27.2−37.7 | | 4 |
| | 2.20[b] | 0.30−0.70 | 30.9−51.7 | | 5 |
| | 2.50[b] | 0.30−0.70 | 32.0−64.0 | | 4 |
| | 6.50 | 6.0−60.0 | | 24.1−221 | 7 |
| | 6.80 | 8.0−80.0 | | 33.6−329 | 7 |
| | 7.10 | 4.0−40.0 | | 15.8−142 | 7 |

[a] In aqueous solution, at 25.0 °C, an ionic strength of 0.2 M, and under the presence of phosphate buffer 0.005 M, unless otherwise stated. [b] Without external buffer. [c] Under the presence of citrate buffer 0.005 M.

substrates (PCITF and NPCITF) in water with the aim of extending our investigations on the aminolysis of chlorothionoformates. Specific aims are the comparisons of these reactions with the following: the pyridinolysis of aryl chloroformates in acetonitrile,[2d] the solvolysis of PCITF,[3] and the phenolysis[4] and aminolysis (secondary alicyclic amines)[5] of the title substrates in water.



PCITF (X = H)
NPCITF (X = $NO_2$)

## Experimental Section

**Materials.** The series of pyridines were purified either by distillation or recrystallization. PClTF was used as purchased. NPClTF was synthesized as described.[5]

**Kinetic Measurements**. These were carried out by means of a diode array spectrophotometer, in aqueous solution, at 25.0 ± 0.1 °C, an ionic strength of 0.2 M (KCl), and usually under the presence of phosphate buffer 0.005 M. In a few cases, the pH was maintained by the corresponding pyridine/pyridinium pair or by the use of citrate buffer 0.005 M. The pH values of some reaction solutions were also measured after completion of these reactions; no significant pH variations were observed within 0.01 pH unit. The reactions were followed at 220−500 nm and carried out under an excess (10-fold at least) of the pyridine over the substrate. The initial substrate concentration was (1−2) × $10^{-5}$ M. Pseudo-first-order rate coefficients ($k_{obsd}$) were found for all the reactions by means of the method described.[6]

In some cases, consecutive reactions were observed: initial fast absorbance increase ($k_{obsd1}$), followed by a slow further increase of absorbance ($k_{obsd2}$), Depending on the experimental conditions, in some reactions the formation and/or hydrolysis of an intermediate could be studied kinetically (see below).

The experimental conditions of the reactions and the values of $k_{obsd1}$ and $k_{obsd2}$ are shown in Tables 1 and 2 and in Tables S1−S4 in Supporting Information.

**Product Studies**. Phenol and 4-nitrophenol (and/or their corresponding anions) were identified as one of the final products of the pyridinolysis of PClTF and NPClTF. This was achieved by comparison of the UV−vis spectra at the end of the reactions with those of authentic samples under the same experimental conditions. For some reactions, the appearance and disappearance of an intermediate was also detected spectrophotometrically at 270−320 nm. As an example, Figure 1 shows a plot of absorbance at 295 nm vs time obtained for the reaction of pyridine with PClTF. We identify this intermediate as the corresponding 1-(aryloxythiocarbonyl)pyridinium cation (intermediate **1** in Scheme 1). Similar intermediates have been detected spectrophotometrically or isolated in the pyridinolysis of methyl chloroformate and other reagents.[7]

A reviewer has pointed out that some catalysis by pyridine of the hydrolysis of the substrates could also take place. Nevertheless, one proof that this catalysis is not important comes from the fact that the final phenol (or 4-nitrophenol, depending on the substrate) concentration for the fast step was never more than 10% of the substrate initial concentration. This was found for the reactions of 4-cyanopyridine, which is the least basic of all the pyridines studied, and therefore this is the most favorable reaction to observe general base catalysis.

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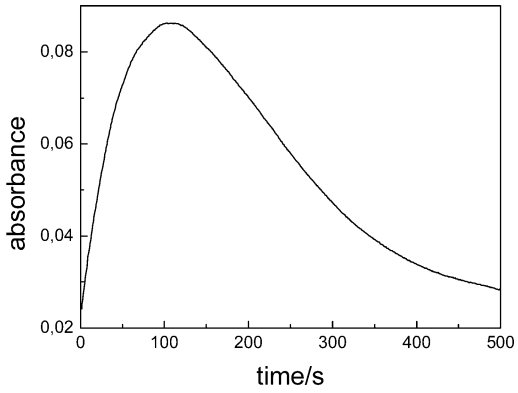
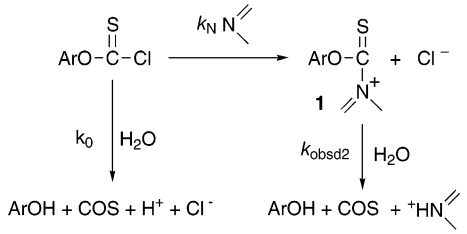



**FIGURE 1.** Plot of absorbance at 295 nm (1-cm cell) against time obtained in the reaction of PClTF with pyridine in aqueous solution at 25.0 °C, ionic strength 0.2 (KCl), $[N]_{tot} = 4 \times 10^{-4}$ M, pH = 6.8 (0.005 M phosphate buffer).

**SCHEME 1**




The above percentage was obtained by comparison of the final absorbance of phenol (before decomposition of intermediate **1**) with an authentic sample of phenol at the same initial substrate concentration, under the same experimental conditions. Namely, the sum of the uncatalyzed term ($k_0$) and the general base-catalyzed term ($k_{gb}$[N]) was at most 10% of the $k_{obsd1}$ value.

## Results and Discussion

**Spectrophotometric Study.** The reactions of PCITF and NPCITF with the series of pyridines were followed spectrophotometrically (220−500 nm), showing, in many cases, a fast absorbance increase, followed by a slower increase. The former increase is attributed to the formation of the corresponding phenol/phenoxide pair ($k_0$ step in Scheme 1) and the latter to the slow hydrolysis of the corresponding thionocarbamate **1** ($k_{obsd2}$ step in Scheme 1), which also produces the corresponding phenol/phenoxide pair. However, the values of $k_{obsd1}$ were obtained by measuring the formation of the thionocarbamate **1** (see below).

In some cases, depending on the pyridine nature and its concentration used, it was possible to obtain kinetic values for the fast reaction ($k_{obsd1}$) or the slow one ($k_{obsd2}$) or both.

**Pyridinolysis of Chlorothionoformates.** The kinetic results obtained for these reactions are in accordance with eqs 1 and 2, where **1**, S, and N represent the corresponding 1-(aryloxythiocarbonyl)pyridinium, the substrate, and the free pyridine, respectively; $[S]_0$ is the initial substrate concentration and $t$ is time. The rate constants $k_0$ and $k_N$ are those for the hydrolysis and pyridinolysis, respectively, of the chlorothionoformates. For all the reactions (except those of both substrates with nicotinamide and that of NPCITF with 4-cyanopyridine),

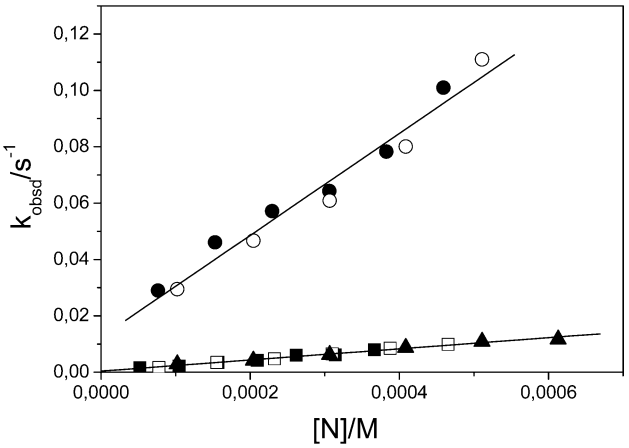



**FIGURE 2.** Plot of $k_{obsd1}$ and $k_{obsd2}$ against free amine concentration for the reaction of 3,4-dimethylpyridine with PClTF, in aqueous solution, at 25.0 °C, ionic strength 0.2 (KCl) (○, $k_{obsd1}$ pH 7.1; ●, $k_{obsd1}$ pH 6.8; ▲, $k_{obsd2}$ pH 7.1; □, $k_{obsd2}$ pH 6.8; ■, $k_{obsd2}$ pH 6.5).

**TABLE 3. Values of p$K_a$ of Pyridinium Ions and of $k_N$ and $k_H$ for the Pyridinolysis of PClTF and NPClTF[a]**

| | | PCITF | | NPCITF | |
|---|---|---|---|---|---|
| pyridine substituent | p$K_a$ | $k_N$[b] ($s^{-1}$ $M^{-1}$) | $k_H$[c] ($s^{-1}$ $M^{-1}$) | $k_N$[b] ($s^{-1}$ $M^{-1}$) | $k_H$[c] ($s^{-1}$ $M^{-1}$) |
| 4-N($CH_3$)$_2$ | 9.87 | 330 | | 673 | |
| 4-$NH_2$ | 9.42 | 222 | | 519 | |
| 3,4-($CH_3$)$_2$ | 6.77 | 181 | 20 | | 75 |
| 4-$CH_3$ | 6.25 | 168 | 15 | | 35 |
| H | 5.37 | 91 | 14 | | 32 |
| 3-$CONH_2$ | 3.4 | | 8 | 123 | 9 |
| 4-CN | 2.2 | | 2 | 100 | 4 |

[a] In aqueous solution, at 25.0 °C, and an ionic strength of 0.2 M. [b] Nucleophilic rate constant for the formation of intermediate **1**. [c] General base-catalyzed (by the corresponding pyridine) rate constant for hydrolysis of intermediate **1**.

the values of $k_0$ were negligible compared to those of the pyridinolysis term in eq 2

$$\frac{d[\mathbf{1}]}{dt} = k_N[N][S] = k_N[N][S]_0\, e^{-(k_{obsd1}\, t)} \quad (1)$$

$$k_{obsd1} = k_0 + k_N[N] \quad (2)$$

The second-order rate coefficients for aminolysis ($k_N$) were obtained as the slopes of plots of eq 2 at constant pH and were pH independent. Figure 2 shows an example of such plots, for $k_{obsd1}$ as well as $k_{obsd2}$. The values of $k_N$ found, together with the p$K_a$ values of the conjugate acids of the pyridines, are shown in Table 3. With these data the Brønsted-type plots of Figure 3 were obtained. Table 3 also shows the values of $k_H$ (obtained from the $k_{obsd2}$ values), which were obtained as explained below.

The slopes of the lines ($\beta$) are 0.07 ± 0.05 and 0.11 ± 0.05 for the reactions of PCITF and NPCITF, respectively. The magnitude of $\beta$ is in agreement with the values of Brønsted slopes found in stepwise mechanisms of similar reactions when the formation of the zwitterionic tetrahedral intermediate ($T^{\pm}$) is the rate-determining step (Scheme 2).[2b,d−f,5,6,8−10]

By applying the steady-state treatment to the intermediate $T^{\pm}$ and assuming that the hydrolysis of com-

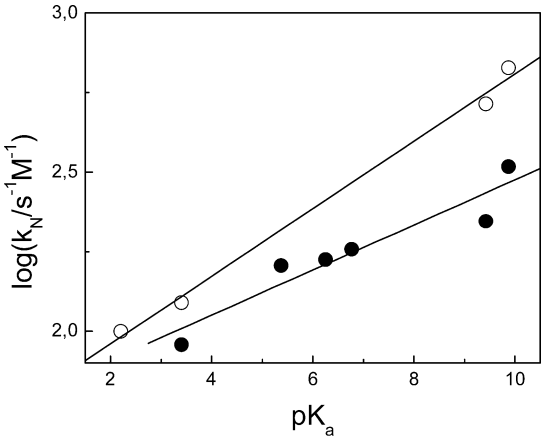
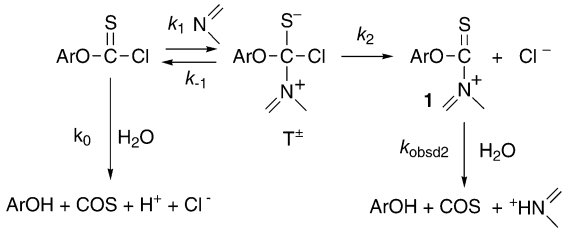



**FIGURE 3.** Brönsted plots for $k_N$, obtained in the reactions of pyridines with PClTF (●) and NPClTF (○), in aqueous solution, 25.0 °C, ionic strength 0.2 (KCl).

**SCHEME 2**




pound **1** is negligible, the following equation results: $k_N = k_1k_2/(k_{-1} + k_2)$, where $k_N$ is the macroscopic nucleophilic rate constant. Since the first step is limiting, it follows that in this scheme, $k_2 \gg k_{-1}$, and therefore, $k_N = k_1$.

As shown in Table 3 and Figure 3, the $k_N$ values for the reactions of NPCITF are greater than those of PCITF. This is reasonable due to the presence of the powerful electron withdrawing 4-nitro group in NPCITF that leaves the thiocarbonyl group of this substrate more reactive than that in PCITF.

For the reactions of the present work, a correlation of log $k_N$ as a function of the p$K_a$ of the conjugate acids of the nucleophile (p$K_N$) and nonleaving group (p$K_{nlg}$) can be achieved by dual regression analysis. This is shown in eq 3 ($R^2 = 0.944$, $n = 10$). Figure 4 shows a double-logarithmic plot of the experimental $k_N$ vs that calculated through eq 3. The slope is unity and the intercept is zero, within experimental errors. The good correlation and unity slope of this plot indicates that the pyridinolysis of PClTF and NPClTF are driven by the same mechanism and the same rate-determining step.

$$\log k_N = (2.4 \pm 0.2) + (0.1 \pm 0.01)pK_N - (0.08 \pm 0.02)pK_{nlg} \quad (3)$$

The pyridinolysis of phenyl and 4-nitrophenyl chloroformates (PCIF and NPCIF, respectively) in acetonitrile obeys a stepwise mechanism, where the formation of a zwitterionic tetrahedral intermediate (T±) is rate determining.[2d] This was shown on the basis of Hammett and

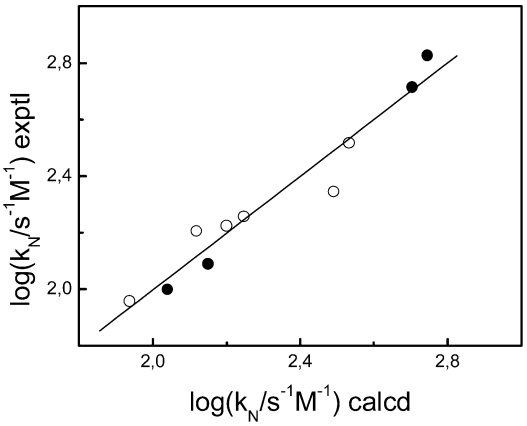



**FIGURE 4.** Double-logarithmic plot of experimental $k_N$ vs calculated $k_N$ (through eq 3) for the reactions of pyridines with PClTF (○) and NPClTF (●), in aqueous solution, 25.0 °C, ionic strength 0.2 (KCl).

Brønsted plots exhibiting low slopes for the nucleophiles (e.g., $\beta \approx 0.3$).[2d] On the other hand, it seems that for these reactions there is little influence of the change of $O^-$ to $S^-$ in the intermediate T±, as judged by the fact that the same step is rate limiting for the aminolyses (secondary alicyclic amines) in water of PCIF and NPCIF[2e] and their corresponding thiono derivatives.[5] Therefore, it is surprising that the same step be rate determining for these reactions in water and acetonitrile, since it is known that amine expulsion from T± ($k_{-1}$ in Scheme 2) is accelerated in less polar solvents[10] and nucleofuge expulsion ($k_2$) is little affected by the solvent.[10] Therefore, comparison of the pyridinolyses of the title substrates in water with those of PCIF and NPCIF in acetonitrile indicates that the change of solvent from water to acetonitrile does not sufficiently increase the value of $k_{-1}$ as to change the rate determining step from formation of T± ($k_1$ step) to its decomposition ($k_2$ step).

On the other hand, substitution of $S^-$ by $O^-$ in the zwitterionic tetrahedral intermediates formed in the aminolysis of phenyl and 4-nitrophenyl 2,4-dinitrophenyl thionocarbonates does affect their stability, due to a faster amine expulsion from the oxy intermediate.[11] Similarly, the zwitterionic intermediate formed in the aminolysis of 3-methyl-7$\beta$-(phenylacetamido)thioxoceph-3-em-4-carboxylic acid expels the amine slower than that from the corresponding oxy intermediate (with $O^-$).[12]

The pyridinolysis of bis(4-nitrophenyl) thionocarbonate (BNPTOC) in water exhibits a linear Brønsted-type plot of slope $\beta = 1.0$, which is consistent with a mechanism through an intermediate T±, where its decomposition to products is the rate-determining step.[13] Comparison with the Brønsted plot obtained for the pyridinolysis of NPCITF (this work), which differs from BNPTOC only in the leaving group, shows that 4-nitrophenoxide is a worse nucleofuge than $Cl^-$ from the tetrahedral intermediate.

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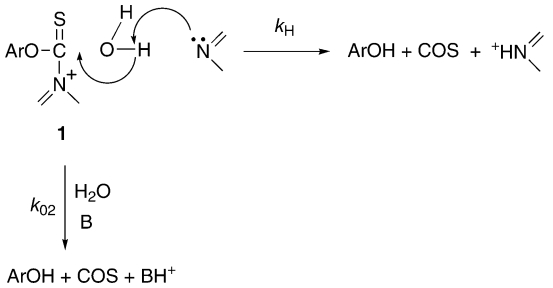
**SCHEME 3**




We have recently found that the pyridinolysis of 2,4-dinitrophenyl phenyl thionocarbonate in water is driven by a stepwise mechanism, with rate-determining formation of a $T^{\pm}$ intermediate at high pyridine basicity ($\beta = 0.1$) and rate-limiting elimination of 2,4-dinitrophenoxide at low pyridine basicity ($\beta = 1.0$).[11] The fact that for the pyridinolysis of PClTF the rate-determining step is the formation of $T^{\pm}$ (this work) indicates that $Cl^-$ is a better nucleofuge from $T^{\pm}$ than 2,4-dinitrophenoxide anion.

The reactions of secondary alicyclic (SA) amines with PCITF and NPCITF show linear Brønsted-type plots with identical slopes, $\beta$ 0.26, indicating that formation of the intermediate $T^{\pm}$ is rate limiting.[5] These results are consistent with the fact that the same step is rate determining for the pyridinolysis of the same substrates (this work), for the following reasons: SA amines are known to be better nucleofuges from the intermediate $T^{\pm}$ than isobasic pyridines.[14] Since for the reactions of these substrates with SA amines $k_{-1} \ll k_2$, this inequality is even more certain for the reactions with isobasic pyridines because the latter are worse leaving groups. This explains why the first step of Scheme 2 is rate limiting for the reactions of PCITF and NPCITF with pyridines.

The rate constants $k_N$ obtained for the pyridinolysis of PCITF and NPCITF (Table 3) are larger than those found for the reactions of these substrates with isobasic SA amines.[5] This is in accordance with the concept of Pearson's hard and soft acids and bases:[15] relatively soft bases such as pyridines would preferably bind to a relatively soft thiocarbonyl group, compared with isobasic SA amines which are relatively harder bases.

For the reactions of phenoxide anions with PClTF and NPCITF in aqueous solution, linear Brønsted-type plots with slopes $\beta = 0.55$ and 0.47, respectively, were found.[4] The values of these slopes and other results were explained by concerted mechanisms, without the formation of a tetrahedral intermediate.[4] This means that substitution of the pyridino moiety in the intermediate $T^{\pm}$ of Scheme 2 by a phenoxy group greatly destabilizes the intermediate. This is consistent with the facts that the pyridinolyses of aryl acetates,[9,16] carbonates,[10,17] and thiolcarbonates[18] are stepwise, whereas the phenolyses of the same substrates are concerted.[19−21]

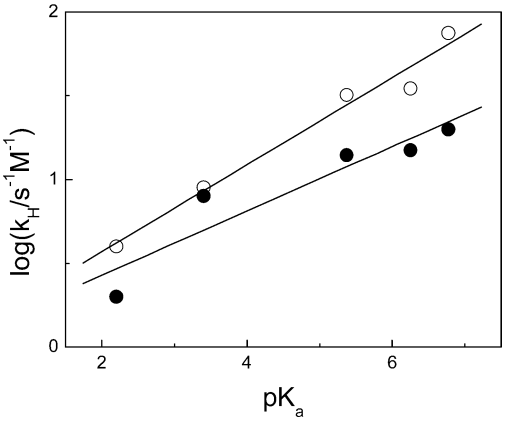



**FIGURE 5.** Bronsted-type plots for the hydrolysis of 1-(phenyloxythiocarbonyl)pyridinium (●) and 1-(4-nitrophenyloxythiocarbonyl)pyridinium (○) cations catalyzed by the corresponding pyridine, in aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl).

The solvolysis of PClTF in water, methanol, ethanol, and aqueous mixtures of the two latter solvents has been subjected to a kinetic investigation.[3b] It was found that these reactions are of $S_N2$ character, especially in water; i.e., a tetrahedral intermediate is not formed.[3b] Comparison with the pyridinolysis of the same substrate (this work) indicates that substitution of a pyridino moiety by OH, MeO, or EtO in the intermediate $T^{\pm}$ of Scheme 2 destabilizes the intermediate. This is in line with the discussion above on the destabilization of the intermediate by the change of a pyridino group by phenoxy. On the other hand, an addition−elimination pathway was proposed for the solvolysis of PClTF in aqueous mixtures of ethanol, methanol, and acetone.[3a] Nevertheless, an $S_N1$ mechanism was claimed to govern the solvolysis of this substrate in aqueous trifluoroethanol mixtures.[3a]

**Hydrolysis of 1-(Aryloxythiocarbonyl)pyridinium (1).** The rate constants for decomposition of these cationic thionocarbamates ($k_{obsd2}$, Tables 1 and 2) show a linear dependence on the corresponding free pyridine (N) concentration, according to eq 4, by analogy to the behavior displayed by chlorothionoformates. The rate constants $k_{02}$ and $k_H$ were obtained as intercept and slope, respectively, of the linear plots of $k_{obsd2}$ vs free amine concentration.

$$k_{obsd2} = k_{02} + k_H[N] \qquad (4)$$

A probable mechanism for the $k_H$ path is water attack to the thiocarbonyl moiety of the thionocarbamate **1**, catalyzed by a pyridine molecule (general base catalysis, rate constant $k_H$), as shown in Scheme 3. The same type of catalysis was reported for the hydrolysis of ring-substituted 1-(methoxycarbonyl)pyridinium cations.[7b] Buffer-catalyzed hydrolysis (rate constant $k_{02}$) can also occur, as shown in Scheme 3 where B is the buffer. The

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latter mechanism would be similar to that for pyridine as catalyst.

Table 3 shows the values of $k_H$ found for the hydrolysis of the various cationic thionocarbamates (**1**). It can be seen that the value of $k_H$ increases as pyridine basicity increases, as expected from general base catalysis. Nevertheless, taking into account that the thionocarbamates studied are obtained "in situ", the kinetic study corresponds to a simultaneous change of the pyridine group of the thionocarbamate and the pyridine catalyst. Figure 5 shows the Brønsted plots for the hydrolysis of the cationic thionocarbamates **1** formed in the pyridinolysis of PClTF and NPClTF. The linear behavior with low slopes ($\beta = 0.19$ and 0.26, respectively) can be explained by the fact that as p$K_a$ increases the effect of a better pyridine catalyst is compensated by a worse leaving pyridine from the corresponding thionocarbamate.

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**Supporting Information Available:** Pages S2−S14 containing Tables S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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