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# Concerted Mechanisms of the Reactions of Phenyl and 4-Nitrophenyl Chlorothionoformates with Substituted Phenoxide Ions

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The title reactions are subjected to a kinetic study in 3% (v/v) dioxane in water, 25.0 °C, ionic strength 0.2 M (KCl). By following the reactions spectrophotometrically, pseudo-first-order rate coefficients ($k_{obsd}$) are found under an excess of the nucleophile. Plots of $k_{obsd}$ vs phenoxide anion concentration at constant pH are linear, with the slope ($k_N$) independent of pH. The Brönsted-type plots (log $k_N$ vs p$K_a$ of the phenols) are linear with slopes $\beta = 0.55$ and 0.47 for the reactions of the phenyl and the 4-nitrophenyl derivatives, respectively. These Brönsted slopes are in agreement with the ones found in the concerted reactions of the same nucleophiles with reactive phenyl esters and acetic anhydride in water. In contrast to the concerted mechanism of the title reactions that of the same substrates with secondary alicyclic amines is stepwise, which means that substitution of an amino moiety in a tetrahedral intermediate with a phenoxy group by another phenoxy group destabilizes the intermediate to the point that it no longer exists.

## Introduction

Although much attention has been focused on the kinetics and mechanism of the hydrolysis,[1] alcoholysis,[2] and aminolysis of chloroformates,[3] little is known on the mechanisms of the reactions of chlorothionoformates.[4]

In the present work, we undergo a kinetic and mechanistic study of the reactions of phenoxide ions with the title substrates (PClTF and NPClTF) with the aim of comparing them with the alcoholysis of substituted phenyl chloroformates[2] and with the aminolysis of the title substrates.[4]

| $C_6H_5OCSCl$ | $4\text{-}NO_2C_6H_4OCSCl$ |
|---|---|
| PClTF | NPClTF |

## Experimental Section

**Materials.** Dioxane (Merck, a.r.) was refluxed over ferrous sulfate and then distilled. The phenols (Aldrich) were purified either by distillation or recrystallization. Phenyl chlorothionoformate (Sigma) was used as purchased. 4-Nitrophenyl chlorothionoformate[4] and bis(phenyl) thionocarbonate[5] (BPTOC) were synthesized as described.

Phenyl 4-nitrophenyl thionocarbonate (PNPTOC) could not be prepared in satisfactory yield by the method reported.[6] This synthesis was as follows: To a solution of 4-nitrophenol (2.02 g, 14.5 mmol) in THF (10 mL) in a Schlenk round-bottomed flask was added a solution (9.1 mL, 14.5 mmol) of 1.6 M butyllithium (Aldrich) slowly under nitrogen atmosphere. The product, lithium 4-nitrophenolate, was rapidly transferred to a compensation funnel, under nitrogen. In another Schlenk round-bottomed flask, phenyl chlorothionoformate (Aldrich, 2.3 g) was dissolved in anhydrous THF (10 mL) under nitrogen and the flask placed in an ethanol−liquid nitrogen bath. The compensation funnel was attached to the flask and the lithium 4-nitrophenolate solution added dropwise with stirring during 2 h. The mixture was left overnight with stirring under nitrogen at ambient temperature. Chloroform (50 mL) was added to this mixture and the solution washed with water. The organic layer was dried with $MgSO_4$ and filtered under vacuum and the solvent evaporated off. The crystallized PNPTOC melted at 187−189 °C (lit.[6] mp 181−182 °C) and was identified as follows: $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.3−7.5 (m, 5H), 7.23 (sd, 2H, $J = 9.2$ Hz), 8.36 (sd, 2H, $J = 9.2$ Hz); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 121.60 (C-2′/6′), 123.27 (C-2/6), 125.48 (C-3/5), 127.2 (C-4′), 129.84 (C-3′/5′), 146.14 (C-4), 153.40 (C-1′), 157.52 (C-1), 193.39 (C═S); IR (KBr) 1487 and 1520 ($CNO_2$), 1225 (C═S), 865 (CH arom mono), 777 and 759 (CH arom disust) $cm^{-1}$.

**Determination of p*K*<sub></sub>$_a$.** The p$K_a$ of the phenols were determined either by spectrophotometric or potentiometric means, in 3% (v/v) dioxane in water, at 25.0 ± 0.1 °C, ionic strength 0.2 M (KCl). The former method was used for 4-methoxy-, H-, 4-chloro-, and 3-chlorophenols at the wavelengths 235, 235, 243, and 240 nm, respectively, using either carbonate or borate buffers, by the method reported.[7]

The potentiometric p$K_a$ measurements were used for 4-cyanophenol and pentafluorophenol under the same conditions as above by the method already described.[5]

**Kinetic Measurements.** These were carried out by means of a Hewlett-Packard 8453 diode array spectrophotometer under the following conditions: 3% (v/v) dioxane in water, at 25.0 ± 0.1 °C, ionic strength 0.2 M (KCl), and phosphate buffer 0.005 M. The pH values of some reaction solutions were checked after completion of the reactions; no significant variations were detected (±0.01 pH units). The reactions of

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**Table 1. Experimental Conditions and $k_{\text{obsd}}$ Values for the Reactions of Phenoxide Anions with Phenyl Chlorothionoformate[a]**

| phenoxide substituent | pH | $10^3[\text{ArOH}]_{\text{tot}}{}^{b}$/M | $10^4 k_{\text{obsd}}$/s$^{-1}$ | no. of runs |
|---|---|---|---|---|
| 4-methoxy | 6.50 | 1.0–10 | 5.1–12 | 6 |
| | 6.80 | 1.0–10 | 6.1–21 | 6 |
| | 7.10 | 0.6–10 | 6.9–34 | 7 |
| none | 6.50 | 1.0–20 | 4.8–7.0 | 6 |
| | 6.80 | 5.0–15 | 6.1–9.4 | 5 |
| | 7.10 | 1.0–15 | 5.6–14 | 6 |
| 4-chloro | 6.50 | 0.2–6.0 | 5.2–13 | 4 |
| | 6.80 | 0.5–4.0 | 7.3–17 | 4 |
| | 7.10 | 0.2–4.0 | 6.3–28 | 4 |
| 3-chloro | 6.50 | 0.5–5.0 | 5.2–8.3 | 5 |
| | 6.80 | 0.3–1.0 | 5.2–7.1 | 5 |
| | 7.10 | 0.3–0.9 | 5.6–9.1 | 4 |
| 4-cyano | 6.50 | 0.5–1.0 | 4.2–6.1 | 4 |
| | 6.80 | 0.5–1.0 | 5.3–9.4 | 4 |
| | 7.10 | 0.5–1.0 | 6.9–16 | 4 |
| pentafluoro | 6.50 | 0.5–5.0 | 12–44 | 5 |
| | 6.80 | 0.5–10 | 14–85 | 7 |
| | 7.10 | 0.7–5.0 | 15–51 | 6 |

[a] In 3% (v/v) dioxane in water at 25.0 °C, ionic strength 0.2 M (KCl), in the presence of phosphate buffer 0.005 M. [b] Total concentration of substituted phenol (acid plus conjugate base).

**Table 2. Experimental Conditions and $k_{\text{obsd}}$ Values for the Reactions of Phenoxide Anions with 4-Nitrophenyl Chlorothionoformate[a]**

| phenoxide substituent | pH | $10^3[\text{ArOH}]_{\text{tot}}{}^{b}$/M | $10^4 k_{\text{obsd}}$/s$^{-1}$ | no. of runs |
|---|---|---|---|---|
| 4-methoxy | 6.50 | 1.0–10 | 7.2–16 | 7 |
| | 6.80 | 1.0–10 | 10–26 | 6 |
| | 7.10 | 0.6–8.0 | 11–33 | 6 |
| none | 6.50 | 1.0–20 | 7.5–25 | 6 |
| | 6.80 | 0.4–15 | 9.4–31 | 7 |
| | 7.10 | 1.0–15 | 13–49 | 6 |
| 4-chloro | 6.50 | 0.2–4.0 | 8.0–15 | 3 |
| | 6.80 | 0.2–4.0 | 8.5–22 | 6 |
| | 7.10 | 0.2–4.0 | 9.8–34 | 6 |
| 3-chloro | 6.50 | 0.3–5.0 | 8.2–14 | 5 |
| | 6.80 | 0.3–1.0 | 8.9–12 | 5 |
| | 7.10 | 0.3–1.0 | 10–16 | 5 |
| 4-cyano | 6.50 | 0.5–1.0 | 9.2–12 | 4 |
| | 6.80 | 0.5–1.0 | 11–17 | 4 |
| | 7.10 | 0.5–1.0 | 17–24 | 4 |
| pentafluoro | 6.50 | 0.5–4.0 | 30–126 | 5 |
| | 6.80 | 0.5–1.7 | 38–75 | 6 |
| | 7.10 | 0.5–2.0 | 34–74 | 5 |

[a] In 3% (v/v) dioxane in water at 25.0 °C, ionic strength 0.2 M (KCl), in the presence of phosphate buffer 0.005 M. [b] Total concentration of substituted phenol (acid plus conjugate base).

**Table 3. Values of p$K_a$ of Phenols and $k_N$ for the Reactions of Phenoxides with Phenyl (PClTF) and 4-Nitrophenyl (NPClTF) Chlorothionoformates[a]**

| nucleophile anion | p$K_a$ of phenol | $k_N$/s$^{-1}$ M$^{-1}$ | |
|---|---|---|---|
| | | PClTF | NPClTF |
| 4-methoxyphenoxide | 10.3 | 491 ± 13 | 543 ± 16 |
| phenoxide | 10.2 | 150 ± 14 | 380 ± 8 |
| 4-chlorophenoxide | 9.6 | 184 ± 7 | 204 ± 6 |
| 3-chlorophenoxide | 9.2 | 71 ± 3 | 102 ± 4 |
| 4-cyanophenoxide | 7.8 | 7.0 ± 0.5 | 11.0 ± 0.4 |
| pentafluorophenoxide | 5.4 | 0.80 ± 0.03 | 3.0 ± 0.2 |

[a] Both p$K$a and $k_N$ values were determined in 3% (v/v) dioxane in water at 25.0 °C, ionic strength 0.2 M (KCl).

phenyl and 4-nitrophenyl chlorothionoformates were followed at 250 nm (disappearance of the substrate) and 350 nm (appearance of the thionocarbonate product), respectively.

All reactions were studied under excess of the phenol over the substrate (10-fold at least). The initial substrate concentration was $2 \times 10^{-5}$ M.

Pseudo-first-order rate coefficients ($k_{\text{obsd}}$) were found for all the reactions, by means of the method reported.[6] The experimental conditions of the reactions and the $k_{\text{obsd}}$ values are shown in Tables 1 and 2.

**Product Studies.** The products of the reactions of phenoxide ion with phenyl and 4-nitrophenyl chlorothionoformates were identified as bis(phenyl) thionocarbonate (PhOCSOPh) and phenyl 4-nitrophenyl thionocarbonate ($\text{PhOCSOC}_6\text{H}_4\text{NO}_2$), respectively. This was achieved by comparison of the UV–vis spectra after completion of the reactions with authentic samples of these products,[7] under the same conditions.

## Results and Discussion

The kinetic law obtained in the present reactions is given by eq 1, where $k_{\text{obsd}}$ is the pseudo-first-order rate coefficient, $k_{\text{O}}$ and $k_{\text{N}}$ are the rate coefficients for hydrolysis and phenolysis, respectively, and ArO$^-$ represents a phenoxide ion. The values of $k_{\text{O}}$ and $k_{\text{N}}$ were obtained as the intercept and slope, respectively, of plots of $k_{\text{obsd}}$ vs [ArO$^-$] at constant pH. Both $k_{\text{o}}$ and $k_{\text{N}}$ values were independent of pH. The $k_{\text{o}}$ values obtained for the reactions of NPClTF and PClTF are $(7.8 \pm 0.2) \times 10^{-4}$ s$^{-1}$ and $(4.2 \pm 0.4) \times 10^{-4}$ s$^{-1}$, respectively; the same values were obtained (within experimental error) in the absence of phenol under the same conditions of buffer and pH. The $k_{\text{N}}$ values are shown in Table 3 together with the p$K_{\text{a}}$ of the phenols. Figure 1 shows the Brönsted-type plots obtained with the data in Table 3.

$$k_{\text{obsd}} = k_{\text{O}} + k_{\text{N}}[\text{ArO}^-] \tag{1}$$

The Brönsted slopes of the plots in Figure 1 are $\beta = 0.55 \pm 0.05$ and $0.47 \pm 0.05$ for the reactions of phenyl and 4-nitrophenyl chlorothionoformates, respectively.

To our knowledge, there are no reports of $\beta$ values for the reactions of phenoxide ions with phenyl chloroformates in water, which could be compared to our values. Nevertheless, there is one report on the reactions of these nucleophiles with ethyl chloroformate in 85% aqueous acetone, where a $\beta$ value of 0.78 is reported, although no firm conclusions regarding the mechanism are drawn.[2a] On the other hand, there are some reports on the alcoholysis of phenyl chloroformates. The methanolysis of these compounds in acetonitrile has been claimed to be concerted,[2b] although the same reactions in water–methanol mixtures are found to be governed by a carbonyl addition–elimination pathway.[2c] The solvolysis of phenyl chloroformate in aqueous ethanol solutions follows an addition–elimination route, with addition being rate determining or possibly an enforced concerted variant.[2d] In aqueous binary mixtures of methanol and ethanol, the solvolysis of *p*-methoxyphenyl chloroformate was found to be consistent with a general base-catalyzed carbonyl addition–elimination mechanism.[2e]

Nevertheless, we can compare the $\beta$ values obtained in this work with those found in the reactions of phenoxide ions with phenyl esters and similar compounds: Our $\beta$ values are in agreement with those for the reactions with 1-acetoxy-8-hydroxynaphthalene ($\beta = 0.48$),[9] 4-chloro 2-nitrophenyl acetate ($\beta = 0.64 \pm 0.05$),[10] acetic anhydride ($\beta = 0.58 \pm 0.05$),[11] 2,4-dinitrophenyl

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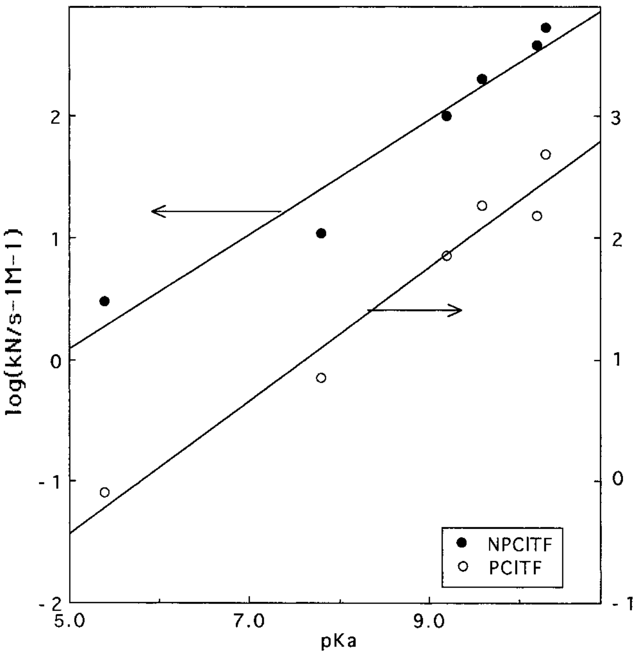


**Figure 1.** Brönsted-type plots obtained in the reactions of phenyl and 4-nitrophenyl chlorothionoformates (PClTF and NPClTF, respectively) with phenoxide anions in 3% (v/v) dioxane in water, 25.0 °C, ionic strength 0.2 M (KCl).

acetate ($\beta = 0.57 \pm 0.03$),[11] 3-nitrophenyl, 4-nitrophenyl, and 3,4-dinitrophenyl formates ($\beta = 0.64$, 0.51, and 0.43, respectively),[12] and the corresponding acetates ($\beta = 0.66$, 0.59, and 0.53, respectively).[12] All these reactions have been found to be governed by concerted mechanisms.[9-12]

Nevertheless, concerted phenolysis mechanisms with larger $\beta$ values are also known, such as those of 4-nitrophenyl, 4-formylphenyl, and 3-nitrophenyl acetates, $\beta =$ 0.75, 0.79, and 1.04, respectively,[10] although these $\beta$ values are based on p$K_a$ values at a different ionic strength (0.1 M) than that of the kinetic measurements (1.0 M).[12]

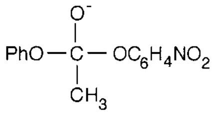
In general, the above concerted mechanisms seem to obey the reactivity–selectivity principle; i.e., the $\beta$ values are larger for the less reactive substrates,[9-12] although there are some exceptions: in the phenolysis of 4-nitrophenyl *N*-methylisonicotinate, a value of $\beta = 0.90$ has been found compared to $\beta = 0.74$ for the reactions of the same nucleophiles with 4-nitrophenyl acetate, despite the higher reactivity of the former substrate.[13]

On the other hand, in solvents less polar than water, larger $\beta$ values are found for the concerted reactions of phenoxides ions: $\beta = 1.32$ and 1.6 for acetic anhydride in acetonitrile and chlorobenzene, respectively.[14]

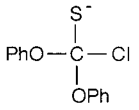
Although the conclusions that some of the above reactions are concerted have been challenged,[15] the arguments given by these authors[15] have been rejected by the original workers.[11,12]

Guthrie has confirmed the conclusions of Williams that the phenolysis of phenyl acetates are concerted, by the application of an extension of Marcus theory to exchange reactions of carboxylic esters.[16] Hengge has reached the same conclusion by measurement of the $^{15}$N isotope effect on the leaving 4-nitrophenoxide ion in the reaction of 4-nitrophenyl acetate with phenoxide anion.[17] The reactions of phenoxide anions with formate esters have been confirmed to be concerted on theoretical grounds.[18]

According to the above results, it seems reasonable that the reactions subjected to the present study are concerted. This conclusion is based on (i) the similar Brönsted slopes found in this work ($\beta_{nuc} = 0.47-0.55$) and those in the concerted reactions of the same nucleophiles with reactive esters and acetic anhydride ($\beta_{nuc} = 0.43-0.68$)[9-12] and (ii) the fact that the tetrahedral intermediate **1** is not formed in the concerted reactions of phenoxide ion with 3- or 4-nitrophenyl acetate, i.e., it is too unstable to exist.[10-16] Therefore, it is very likely that the putative intermediate formed in the phenolysis of phenyl chlorothionoformate (this work, **2**) be much more unstable than **1** for the following reasons:

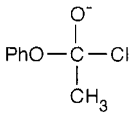

$\mathrm{PhO{-}C(O^-)(CH_3){-}OC_6H_4NO_2}$

**1**

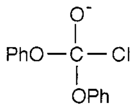

$\mathrm{PhO{-}C(S^-)(OPh){-}Cl}$

**2**

The change of 3- or 4-nitrophenoxy by Cl should render intermediate **3** more unstable kinetically than **1** in view of the superior nucleofugality of Cl compared to the other groups. Substitution of methyl by phenoxy should result in a further destabilization of intermediate **4** since it is known that the similar change of methyl by methoxy or ethoxy renders the tetrahedral intermediates more unstable.[19] On the other hand, the change of $O^-$ to $S^-$ in a tetrahedral intermediate should stabilize the intermediate,[19c,20] although this stabilization should not be enough to compensate for the greater destabilization caused by the other two groups. Moreover, Williams has argued that the presence of two phenoxy (or substituted phenoxy) groups attached to the central carbon of a tetrahedral intermediate is sufficient to destabilize this species in such way as to prevent its existence.[21]


$\mathrm{PhO{-}C(O^-)(CH_3){-}Cl}$

**3**


$\mathrm{PhO{-}C(O^-)(OPh){-}Cl}$

**4**

Obviously, substitution of one of the PhO groups in **2** by 4-nitrophenoxy should destabilize the "intermediate" further, so that the reactions of phenoxide ions with 4-nitrophenyl chlorothionoformate should also be concerted.

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It has been claimed that thioanion attack on phenyl acetates and phenyl thiolacetates can involve the participation of a tetrahedral intermediate.[21] When the formation of this is rate determining a $\beta_{\mathrm{nuc}} = 0.3$ has been obtained.[22] In the reactions described in the present work, if a tetrahedral intermediate were formed its formation would be rate limiting because chloride ion is a very powerful nucleofuge, and therefore, its expulsion from the putative intermediate would be faster than expulsion of phenoxide anions. The fact that in the present reactions $\beta_{\mathrm{nuc}}$ is 0.47−0.55 is not in agreement with a stepwise process with formation of a putative tetrahedral intermediate as the rate-determining step.

In contrast to the concerted reactions exhibited by the title substrates with phenoxide ions, the reactions of the same substrates with secondary alicyclic amines are known to proceed by stepwise mechanisms.[4] In other words, substitution of one of the PhO groups in the putative intermediate **2** by a secondary amino group should stabilize the "intermediate" and make possible its existence as a discrete species. This is in accord with the arguments by Williams concerning the stability of different tetrahedral intermediates.[21]

The fact that the reactions of phenyl chlorothionoformates with aryl oxide anions are concerted while those with amines are stepwise is in agreement with the behavior exhibited by the reactions of phenyl esters and acetic anhydride. The reactions of phenyl acetates,[10−13,21] benzoates[11,23] and formates,[12] as well as those of acetic anhydride[11] with phenoxide ions, are concerted, in contrast to those with amines that are known to proceed through a tetrahedral intermediate in a two-step reaction.[24] This confirms that substitution of an amino moiety in a tetrahedral intermediate that possesses a phenoxy group by another phenoxy group brings about such destabilization that the intermediate no longer exists; i.e., its lifetime becomes shorter than a vibration period.[25]

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