

# Kinetic investigation of the phenolysis of phenyl 4-nitrophenyl and phenyl 2,4-dinitrophenyl carbonates

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The reactions of phenyl 4-nitrophenyl carbonate (PNPC) and phenyl 2,4-dinitrophenyl carbonate (PDNPC) with a homogeneous series of phenoxide anions are subjected to a kinetic investigation in water at 25.0 °C, ionic strength 0.2 mol dm<sup>-3</sup> (KCl). Under phenoxide or total phenol excess over the substrate all these reactions obey pseudo first-order kinetics and are first order in phenoxide. The Brønsted-type plots for the nucleophilic rate constants are linear with slopes 0.61 and 0.49 for the phenolysis of PNPC and PDNPC, respectively. The magnitude of these slopes and the absence of curvature in the Brønsted plot at pK<sub>a</sub> = 7.1 for the PNPC reactions are consistent with concerted mechanisms (one step) for both reaction series. PDNPC is more reactive than PNPC toward phenoxide nucleophiles; this can be explained by the presence of a second nitro group in PDNPC, which (i) leaves its carbonyl carbon more positively charged than that of PNPC, making the former a better electrophile, and (ii) makes 2,4-dinitrophenoxide a better leaving group than 4-nitrophenoxide. The larger nucleophilic rate coefficients found in this work relative to those obtained in the concerted phenolysis of 4-nitrophenyl and 2,4-dinitrophenyl methyl carbonates is explained by a stronger electron withdrawal from PhO compared to MeO. Comparison of the concerted phenolysis of PNPC with the stepwise reactions of quinuclidines with the same substrate indicates that substitution of a quinuclidino group in a zwitterionic tetrahedral intermediate by a phenoxy group greatly destabilises the intermediate.

## Introduction

Although the kinetics and mechanisms of the aminolysis of esters and carbonates and their thio derivatives have been the subject of numerous investigations,<sup>1</sup> the phenolysis of these compounds have been less studied. Among the latter, there have been some reports on the mechanism of the phenolysis of esters and thioesters;<sup>2–5</sup> nevertheless, the mechanisms of the phenolysis of thiocarbonates and carbonates have received little attention.<sup>6,7</sup> Furthermore, to our knowledge, there are no reports on the kinetics and mechanism of the phenolysis of diaryl carbonates.

Recently we have studied kinetically the phenolysis of *S*-(4-nitrophenyl), *S*-(2,4-dinitrophenyl), and *S*-(2,4,6-trinitrophenyl) ethyl thiocarbonates (NPTC, DNPTC, and TNPTC respectively).<sup>6</sup> In this work linear Brønsted-type plots were obtained, which were interpreted through a concerted reaction path.<sup>6</sup>

We have also performed a mechanistic study of the phenolysis of 4-nitrophenyl, 2,4-dinitrophenyl and 2,4,6-trinitrophenyl methyl carbonates (NPC, DNPC and TNPC, respectively), where concerted mechanisms were proposed on the basis of the Brønsted-type plots obtained.<sup>7</sup>

On the other hand, Gresser and Jencks have kinetically examined the reactions of quinuclidines (tertiary alicyclic amines) with phenyl aryl carbonates.<sup>1c</sup> Based on the sharp curvature of the Brønsted-type plots obtained, they concluded that these reactions are stepwise, through the formation of a zwitterionic tetrahedral intermediate (T<sup>±</sup>).<sup>1c</sup> They also studied the influence of the amine nature on the stability of the intermediate T<sup>±</sup>, and found that quinuclidines destabilise T<sup>±</sup> in comparison with other isobasic amines.<sup>1c</sup>

The reactions of quinuclidines with NPTC are stepwise,<sup>8</sup> in contrast to the concerted reactions of phenoxides with the same substrate.<sup>6</sup> This is an indication that substitution of a quinuclidine in T<sup>±</sup> by a phenoxy group destabilises this intermediate.

In order to extend our mechanistic investigations toward the phenolysis of aryl carbonates we perform in the present work a kinetic study of the phenolysis of phenyl 4-nitrophenyl and phenyl 2,4-dinitrophenyl carbonates (PNPC and PDNPC, respectively).

The object of this work is four-fold. (i) To investigate the mechanism of the phenolysis of aryl carbonates. (ii) To verify the destabilising effect of a phenoxy substituent in a tetrahedral intermediate relative to a quinuclidino or other amino groups. (iii) To assess the influence of the non-leaving group of the substrate on the kinetics and mechanisms, and particularly on the stability of the tetrahedral intermediate, by comparing the title reactions with the phenolyses of NPC,<sup>7</sup> DNPC,<sup>7</sup> 4-nitrophenyl acetate,<sup>3a,5</sup> and 2,4-dinitrophenyl acetate.<sup>3b,c</sup> (iv) To investigate the effect of the leaving group basicity on these mechanisms by comparing the kinetics of the phenolysis of PNPC with that of PDNPC (leaving groups: 4-nitrophenoxide and 2,4-dinitrophenoxide, respectively).

## Experimental

### Materials

The phenols were purified by distillation or recrystallization. Phenyl 4-nitrophenyl carbonate (PNPC) and phenyl 2,4-dinitrophenyl carbonate (PDNPC) were synthesised by a modification of a standard procedure,<sup>1c</sup> as follows. To a solution of 4-nitrophenol or 2,4-dinitrophenol (1.6 mmol) dissolved in THF (20 ml) in a Schlenk round-bottomed flask, a solution (1.1 ml) of 1.6 mol dm<sup>-3</sup> butyllithium (Aldrich) was added slowly under a nitrogen atmosphere. The product, the corresponding lithium aryloxide, was transferred to a compensation funnel, under nitrogen, and added to a solution of phenyl chloroformate (0.22 ml, Aldrich) in anhydrous THF (20 ml) in an ethanol–liquid nitrogen bath at about –50 °C. The addition was dropwise to a stirred solution over a period of 2 h. The temperature was

**Table 1** Experimental conditions and  $k_{\text{obs}}$  values for the reactions of phenoxide anions with phenyl 4-nitrophenyl carbonate (PNPC)<sup>a</sup>

Phenoxide substituent	pH	$10^3[\text{ArOH}]_{\text{tot}}/\text{mol dm}^{-3b}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	Number of runs
4-Methoxy	10.0	0.50–3.0	7.80–23.3	5
	10.3	0.50–3.0	10.2–33.5	5
	10.6	0.50–3.0	16.5–44.3	5
None	9.6	2.0–20	7.20–50.0	5
	9.9	2.0–20	9.10–68.0	5
	10.2	2.0–20	14.7–96.5	5
3-Chloro	8.7	2.0–20	4.30–33.1	5
	9.0	2.0–20	7.01–49.6	5
	9.3	2.0–20	8.20–68.7	5
4-Cyano	7.5	20–80	7.90–22.7	5
	7.8	20–80	11.1–38.0	5
	8.1	20–80	15.7–48.1	5
2,6-Difluoro	8.7 <sup>c</sup>	2.0–10	1.08–3.31	5
	9.0 <sup>c</sup>	2.0–10	1.12–3.46	5
	9.3 <sup>c</sup>	2.0–10	1.16–3.37	4
Pentafluoro	6.7 <sup>d</sup>	30–70	0.502–1.08	5
	7.0 <sup>d</sup>	30–70	0.530–1.11	5
	7.3 <sup>d</sup>	30–70	0.593–1.16	5

<sup>a</sup> In water, at 25.0 °C, ionic strength 0.2 mol dm<sup>-3</sup> (KCl). <sup>b</sup> Total concentration of substituted phenol (acid plus conjugate base). <sup>c</sup> Borate buffer 0.01 mol dm<sup>-3</sup>. <sup>d</sup> Phosphate buffer 0.01 mol dm<sup>-3</sup>.

**Table 2** Experimental conditions and  $k_{\text{obs}}$  values for the reactions of phenoxide anions with phenyl 2,4-dinitrophenyl carbonate (PDNPC)<sup>a</sup>

Phenoxide substituent	pH	$10^3[\text{ArOH}]_{\text{tot}}/\text{mol dm}^{-3b}$	$10^2 k_{\text{obs}}/\text{s}^{-1}$	Number of runs
4-Methoxy	9.4 <sup>c</sup>	0.40–5.0	0.60–4.46	6
	9.7 <sup>c</sup>	0.30–5.0	1.27–9.30	7
	10.0 <sup>c</sup>	0.40–5.0	2.50–16.0	6
None	9.6	0.20–3.0	1.05–6.74	6
	9.9	0.20–3.0	2.20–10.0	6
	10.2	0.20–3.0	2.77–14.1	6
3-Chloro	8.7	1.0–40	0.476–17.3	8
	9.0	1.0–40	0.914–25.9	8
	9.3	1.0–40	1.34–28.7	8
4-Cyano	7.5	2.5–50	0.440–10.0	8
	7.8	1.0–50	0.550–11.0	8
	8.1	2.5–50	0.720–16.2	8
2,6-Difluoro	6.8	1.0–40	0.072–2.0	8
	7.1	1.0–40	0.100–3.52	8
	7.4	1.0–40	0.153–4.78	8
Pentafluoro	8.0 <sup>c</sup>	6.0–80	0.272–2.65	6
	8.5 <sup>c</sup>	6.0–80	0.280–2.20	5
	9.0 <sup>c</sup>	6.0–80	0.330–3.05	6

<sup>a</sup> In water, at 25.0 °C, ionic strength 0.2 mol dm<sup>-3</sup> (KCl). <sup>b</sup> Total concentration of substituted phenol (acid plus conjugate base). <sup>c</sup> Borate buffer 0.01 mol dm<sup>-3</sup>.

maintained during the addition by adding liquid nitrogen to the bath occasionally. 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 over MgSO<sub>4</sub>, filtered under vacuum and the solvent removed by evaporation. PNPC mp 129–130 °C (from diethyl ether) (lit.,<sup>1c</sup> 128–129 °C). PDNPC mp 110–111 °C (from diethyl ether) (lit.,<sup>1c</sup> 108–110 °C).

### Kinetic procedures

These were performed spectrophotometrically by following the production of 4-nitrophenoxide or 2,4-dinitrophenoxide ions at 400 nm through a Hewlett-Packard 8453 diode array spectrophotometer. The reactions were studied in aqueous solutions at 25.0 ± 0.1 °C, ionic strength 0.2 mol dm<sup>-3</sup> (maintained with KCl), and with at least a 10-fold excess of total phenol over the substrate. The initial concentration of the substrates was 3 × 10<sup>-5</sup> mol dm<sup>-3</sup> in all the reactions.

For the preparation of the kinetic samples with no external buffer (see Tables 1 and 2) a different stock solution of the corresponding phenol (with phenoxide fractions of ca. 0.33,

0.50, 0.67) was used for each pH. Different aliquots of these stock solutions were poured into 10 ml volumetric flasks, together with the corresponding volume of a KCl stock solution, to keep the total ionic strength at 0.2 mol dm<sup>-3</sup>. The desired pH was obtained by addition of one or two drops of a stock solution of KOH or HCl before filling up the flask. The pH was also measured at the end of some runs; the difference between the initial and final pH values was always smaller than 0.03.

Pseudo-first-order rate coefficients ( $k_{\text{obs}}$ ) were found in all cases. The experimental conditions of the reactions and the  $k_{\text{obs}}$  values obtained are shown in Tables 1 and 2.

### Product studies

4-Nitrophenoxide and 2,4-dinitrophenoxide anions were identified as one of the products of the title reactions by comparison of the UV–VIS spectra after completion of some of these reactions with those of authentic samples of 4-nitrophenol and 2,4-dinitrophenol under the same experimental conditions.

In the reactions of both substrates with phenol, the presence of diphenyl carbonate, (PhO)<sub>2</sub>CO, in the reaction media was

**Table 3** Values of  $pK_a$  of phenols and  $k_N$  for the reactions of phenoxides with diaryl carbonates<sup>a</sup>

Phenoxide substituent	$pK_a$ of phenol	$k_N/s^{-1} (\text{mol dm}^{-3})^{-1}$	
		PNPC	PDNPCC
4-Methoxy	10.3	$19 \pm 1$	$90 \pm 2$
None	9.9	$7.0 \pm 0.2$	$63 \pm 3$
3-Chloro	9.0	$5.0 \pm 0.1$	$12.7 \pm 0.2$
4-Cyano	7.8	$0.88 \pm 0.03$	$4.2 \pm 0.1$
2,6-Difluoro	7.1	$0.29 \pm 0.01$	$1.78 \pm 0.03$
Pentafluoro	5.3	$0.013 \pm 0.001$	$0.33 \pm 0.01$

<sup>a</sup> Both  $pK_a$  and  $k_N$  values were determined in water, at 25.0 °C, ionic strength 0.2 mol dm<sup>-3</sup> (KCl).

determined by HPLC comparison of an authentic sample (Sigma) with those after completion of some reactions under the same experimental conditions. HPLC characteristics: column Eurospher C-18 (10 cm, 7  $\mu\text{m}$ ), eluant acetonitrile–water 70 : 30, isocratic mode 0.7 ml min<sup>-1</sup>.

## Results and discussion

The rate law obtained for all the reactions under investigation is given by eqns. (1) and (2), where P is 4-nitrophenoxide or

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

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

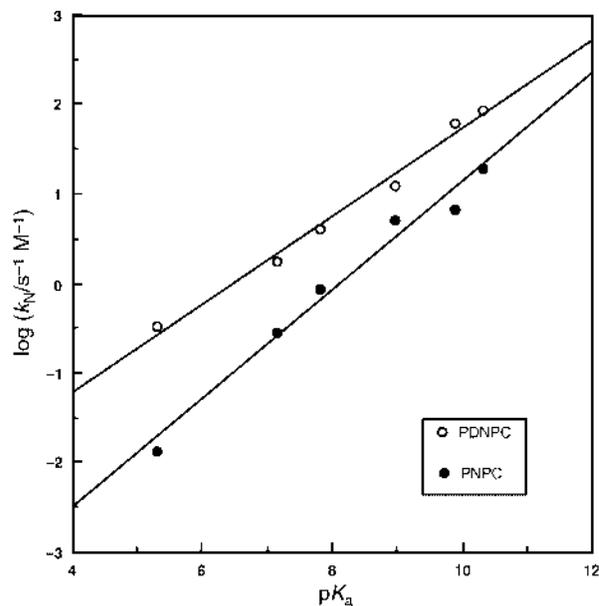
2,4-dinitrophenoxide, S represents the substrate (either PNPC or PDNPC) and  $k_{\text{obs}}$  is the pseudo-first-order rate coefficient (excess of substituted phenoxide or total phenol over the substrate was used throughout). In eqn. (2),  $k_0$  and  $k_N$  are the rate coefficients for hydrolysis and phenolysis of the substrates, respectively, and  $\text{ArO}^-$  represents the substituted phenoxide nucleophile.

Linear plots of  $k_{\text{obs}}$  vs.  $[\text{ArO}^-]$  at constant pH were found for the reactions of both substrates. The  $k_0$  values (intercept of the plots) were much smaller than the phenolysis term in eqn. (2) and subjected to large errors. The nucleophilic rate constants ( $k_N$ ) were obtained as the slopes of these plots, and their values are shown in Table 3. The Brønsted-type plots, obtained with these values and the  $pK_a$  of the phenols, are shown in Fig. 1.

The plots in Fig. 1 are both linear with slopes  $\beta = 0.61$  and 0.49, and correlation coefficients  $R = 0.9894$  and 0.9950, for the phenolysis of PNPC and PDNPC, respectively. The magnitudes of these Brønsted slopes are consistent with concerted mechanisms. Similar values for the slopes of Brønsted plots have been found in the concerted phenolyses of 4-nitrophenyl and 3,4-dinitrophenyl acetates ( $\beta = 0.59$  and 0.53, respectively),<sup>5,9</sup> 4-nitrophenyl and 3,4-dinitrophenyl formates ( $\beta = 0.51$  and 0.43, respectively),<sup>5</sup> 2,4-dinitrophenyl acetate ( $\beta = 0.57$ ),<sup>3c</sup> and aryl methyl carbonates with aryl = 4-nitrophenyl, 2,4-dinitrophenyl and 2,4,6-trinitrophenyl ( $\beta = 0.67$ , 0.48 and 0.52, respectively).<sup>7</sup>

Analogous Brønsted slopes are reported in the concerted aminolysis of some related compounds: linear Brønsted plots with slopes  $\beta = 0.56$  and 0.48 are exhibited in the reactions of secondary alicyclic amines with *S*-(2,4-dinitrophenyl) and *S*-(2,4,6-trinitrophenyl) ethyl thiolcarbonates.<sup>10</sup> Also, methoxycarbonyl transfer between isouquinoline and pyridines shows a linear Brønsted plot of slope  $\beta = 0.58$ .<sup>11</sup>

The instability of the putative anionic tetrahedral intermediate formed in the reactions of phenoxide anions with PNPC and PDNPC should be extremely high in view of the three *O*-aryl groups attached to the central carbon of the intermediate. Williams and co-workers have argued that two *O*-aryl groups are sufficient to destabilise anionic tetrahedral intermediates to the point of nonexistence.<sup>3a</sup> Therefore, introduction of a third one should further destabilise this “intermediate” and perhaps



**Fig. 1** Brønsted-type plots obtained in the phenolysis of phenyl 4-nitrophenyl carbonate (PNPC) and phenyl 2,4-dinitrophenyl carbonate (PDNPC), in aqueous solution at 25.0 °C, ionic strength 0.2 mol dm<sup>-3</sup>. The slopes are  $\beta = 0.61$  and 0.49, respectively.

render its lifetime comparable to a vibration period (*ca.* 10<sup>-13</sup> s). Hence the intermediate would not be formed (it would be too unstable to exist) and the concerted mechanism should be enforced.<sup>12</sup>

The linearity of the Brønsted plot and the value of its slope are not enough to prove a concerted mechanism. The best demonstration of a concerted process is the lack of a Brønsted break at the  $pK_a$  expected for a change in rate-determining step if the reaction were stepwise.<sup>12</sup> If the phenolysis of PNPC were stepwise, the breakpoint of the Brønsted plot would be at  $pK_a = 7.1$ , which corresponds to the  $pK_a$  of 4-nitrophenol. As seen in Fig. 1, there is no such break in the Brønsted plot for PNPC. The absence of this break shows that the mechanism is concerted.<sup>12</sup>

For the phenolysis of PDNPC the centre of the Brønsted curvature (breakpoint) for a stepwise reaction should be at  $pK_a = 4.1$  ( $pK_a$  of 2,4-dinitrophenol). Unfortunately this point lies beyond the  $pK_a$  range used in this investigation. Nonetheless, if the mechanism is concerted for the phenolysis of PNPC it would certainly be concerted for the same reactions of PDNPC, in view of the better nucleofuge involved in the latter “intermediate”, which would make it even more unstable.

The greater reactivity of PDNPC than PNPC toward phenoxides (Table 3 and Fig. 1) could be explained by the presence of a second nitro group in the former substrate, which leaves the carbonyl carbon more positive, and therefore, more prone to nucleophilic attack. Furthermore, since the second nitro group is in the leaving group of PDNPC, this nucleofuge should be expelled faster from PDNPC than 4-nitrophenoxide from PNPC.

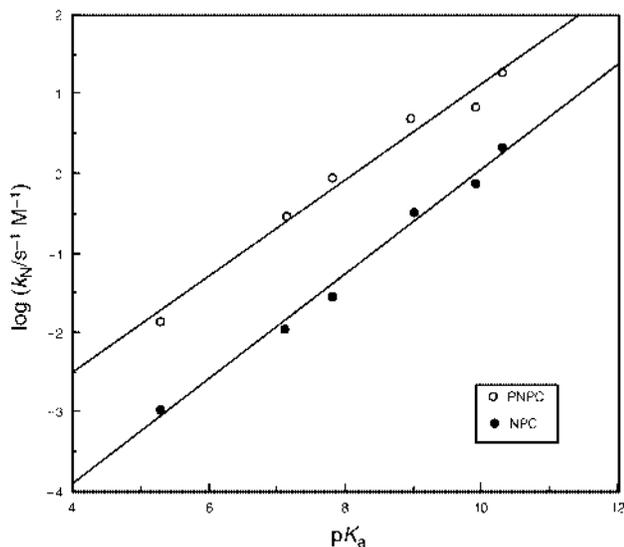


Fig. 2 Brønsted-type plots obtained in the phenolysis of phenyl 4-nitrophenyl carbonate (PNPC) and methyl 4-nitrophenyl carbonate (NPC), in aqueous solution at 25.0 °C, ionic strength 0.2 mol dm<sup>-3</sup>.

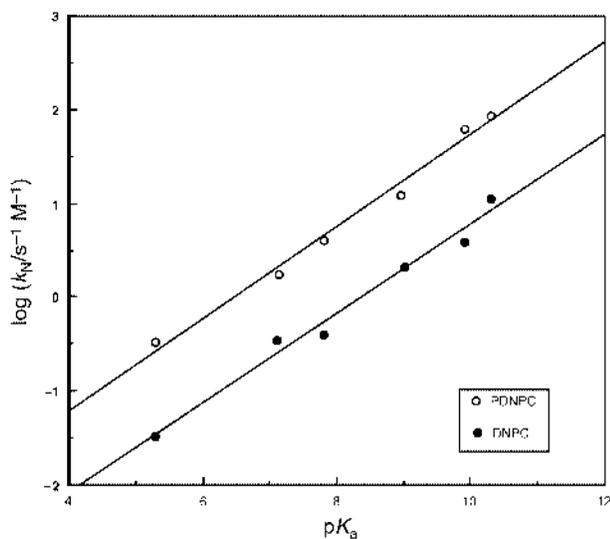


Fig. 3 Brønsted-type plots obtained in the phenolysis of phenyl 2,4-dinitrophenyl carbonate (PDNPC) and methyl 2,4-dinitrophenyl carbonate (DNPC), in aqueous solution at 25.0 °C, ionic strength 0.2 mol dm<sup>-3</sup>.

The phenolyses of 4-nitrophenyl and 2,4-dinitrophenyl methyl carbonates (NPC and DNPC, respectively) are concerted, as indicated by the lack of a Brønsted break at  $pK_a$  7.1 for the former reactions.<sup>7</sup> Fig. 2 shows a comparison between the Brønsted plots for the phenolysis of PNPC and NPC, while Fig. 3 exhibits those plots for the phenolysis of PDNPC and DNPC. From these figures it can be seen that there is a remarkable increase of the nucleophilic rate constant by introducing phenoxy in place of methoxy as the nonleaving group of the substrate. This must arise from the stronger electron-

withdrawing inductive effect of the phenoxy group ( $\sigma_I = 0.37$ )<sup>13</sup> compared to methoxy ( $\sigma_I = 0.29$ )<sup>13</sup> and the smaller electron donation by resonance of phenoxy ( $\sigma_R = -0.40$ )<sup>13</sup> relative to methoxy ( $\sigma_R = -0.56$ ).<sup>13</sup> These effects should increase the positive charge on the carbonyl carbon of PNPC, relative to that of NPC, facilitating therefore the nucleophile attack toward the former substrate, compared to NPC.

The fact that the reactions of PNPC and PDNPC with phenoxide anions are concerted (this work) whereas those of the same substrates with quinuclidines are stepwise<sup>1c</sup> shows that the zwitterionic tetrahedral intermediate formed in the latter reactions is greatly destabilised by the change from a quinuclidino to a phenoxy group. This result is in line with the facts that the reactions of ethyl *S*-(4-nitrophenyl) thiocarbonate with phenoxide anions are concerted,<sup>6</sup> whereas those of the same substrate with quinuclidines are stepwise.<sup>8</sup>

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