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# Kinetics of the reaction of phenyl picrates with phenoxide ions in water. Concerted or stepwise?<sup>†‡</sup>

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A kinetic study is reported of the exchange reactions of substituted phenoxide ions with some ring-substituted 2,4,6-trinitrophenyl ethers in water. The  $\beta$ rønsted diagrams formed by plotting log k, where k is the second-order rate constant for reaction, versus pK<sub>a</sub> show a distinct change in slope when  $\Delta pK_a = 0$  ( $\Delta pK_a$  being the difference in  $pK_a$  values of the leaving group and nucleophile). This is consistent with a two-step process involving a discrete  $\sigma$ -adduct intermediate rather than a concerted process. From the measured  $\beta$  values for forward and reverse processes, the overall effective charge map has been constructed. Copyright © 2013 John Wiley & Sons, Ltd. Supporting information may be found in the online version of this paper.

Keywords: βrønsted equation; effective charge map; intermediates; nitro-compounds; nucleophilic aromatic substitution

There is considerable evidence that most reactions proceeding by the  $S_{\rm N}Ar$  mechanism of nucleophilic aromatic substitution involve an intermediate sitting in a potential energy well. The two-step Addition–Elimination mechanism postulated by Bunnett<sup>[1]</sup> is well documented in the literature.<sup>[2]</sup> The successful identification by NMR of intermediates such as (1), known as Meisenheimer Complexes or  $\sigma$ -adducts, on the substitution pathway offers significant support to the proposed mechanism.<sup>[3–5]</sup> Also, detailed kinetic studies of leaving group effects and base catalysis can only be understood in terms of the presence of intermediates.<sup>[6]</sup>

An alternative mechanism for nucleophilic aromatic substitution is one that involves a concerted pathway in which there is a single transition state, i.e. transformation from a two-step to a one-step process, without the presence of an intermediate. Evidence for this pathway comes from kinetic studies of the displacement of the 4-nitrophenoxide ion from 2-(4-nitrophenoxy)-4,6-dimethoxy-1,3,5-triazine by substituted phenoxide ions in aqueous solution,<sup>[7,8]</sup> Eqn (1). Here, the possible intermediate is regarded as being so unstable that it



is replaced by a transition state.<sup>[9]</sup> A linear  $\beta$ rønsted plot of *log k*, where *k* represents the second-order rate constant for displacement, versus pK<sub>a</sub> values was observed. The pK<sub>a</sub> values are for the parent phenols from which the nucleophiles are derived. The linearity of the plot extended to pK<sub>a</sub> values both above and below that of the leaving group, 4-nitrophenol, and this linearity is evidence for a concerted process.

In fact, there is good evidence that several nucleophilic substitutions on esters and other acyl compounds, including the reaction of 4-nitrophenyl acetate with aryloxide ions,<sup>[10]</sup> are concerted one-step processes.<sup>[11,12]</sup> However, the reaction of 4-nitrophenoxy derivatives of Fischer carbenes with aryloxide ions has been shown to proceed by a stepwise mechanism.<sup>[13]</sup>

Here, we report a kinetic study of the reactions, in aqueous solution, of some ring-substituted 2,4,6-trinitrophenyl ethers, **2**, with a series of substituted phenoxide ions, **3**. The  $\beta$ rønsted diagrams formed when plotting *log k* versus pK<sub>a</sub> show a distinct change in slope when  $\Delta pK_a = 0$  ( $\Delta pK_a$  being the difference in  $pK_a$  values of the leaving group and nucleophile). This is consistent with a two-step process involving a discrete  $\sigma$ -adduct intermediate **4** as shown in Eqn (2). From the measured  $\beta$  value for both forward and reverse processes, the effective charges have been determined, and the overall effective charge map constructed.<sup>[14]</sup>

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- <sup>+</sup> This paper is in memory of Professor Rory More O'Ferrall, a fine chemist and a gentleman.
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Figure 1. Dependence of  $k_{obs}$  on phenoxide concentration for the reactions of 2(a) with phenoxide, 4-bromophenoxide and 2-chloro-4-methylphenoxide ions



**<sup>2</sup>**(b)  $R^1 = NO_2$ ,  $R^2 = NO_2$ **2**(c)  $R^1 = H$ ,  $R^2 = NO_2$ 

## **RESULTS AND DISCUSSION**

The rate constants for reaction of various ring-substituted phenoxide ions, in phenol/phenoxide buffers, with five different phenyl-2,4,6-trinitrophenyl ethers, 2(a-e), were measured in agueous solution at 25 °C. The addition of dioxan (5-10%, v/v) was required to aid solubility, but the dioxan proportion was kept constant for each substrate. A series of buffer solutions was prepared with various phenoxide concentrations but at constant pH, and with ionic strength maintained at 0.1 mol  $dm^{-3}$  with sodium chloride. Reactions were initiated by addition of the substrate solution to a prepared sample in the thermostatted cell compartment of a conventional spectrophotometer. For faster reactions, stopped-flow spectrophotometry was used, and for very slow reactions, a sampling technique (experimental section) was used. Reactions were monitored by the appearance of the appropriate leaving group, e.g. 4-nitrophenoxide from 2(a), at a wavelength between 360 and 400 nm. Typical data are in Fig. 6 (supplementary information). There was no evidence for the accumulation of either intermediates, or of other adducts not on the reaction pathway<sup>[2,4,5]</sup> during these processes. All kinetic measurements were made under first-order conditions with the buffer concentration (PhOH/PhO-) in large excess of the substrate concentration  $(2 \times 10-5 \text{ mol } \text{dm}^{-3})$ . A typical trace is shown in Fig. 7 (supplementary information). First-order rate constants,  $k_{obs}$ , were calculated with correlation coefficients 0.992-0.999 by standard techniques.

At constant pH, values of  $k_{obs}$  were found to increase linearly with the phenoxide concentration as shown in Fig. 1. The gradients of these plots give the values of the second-order rate constants,  $k_{s_i}$  for the forward reaction shown in Eqn (2). Generally, buffer ratios PhOH/PhO- were kept close to 1:1. Changing the buffer ratio to 2:1 did not affect the values obtained for  $k_s$ , within experimental error, indicating that interference from hydroxide ions was not a problem. Data for reactions of 2(a), leaving group<sup>[15]</sup> pK<sub>a</sub> 7.12, are in Table 1.

<b>Table 1.</b> Kinetic data <sup>a</sup> for the reacti	ons of <b>2</b> (a) with substitute	d phenoxide ions at 25 °C
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Substituents in <b>3</b>	рК <sub>а</sub> ь	$k_{\rm s}/{\rm dm}^3~{\rm mol}^{-1}~{\rm s}^{-1}$	рН	[3]/10 <sup>-2</sup> mol dm <sup>-3</sup>	$k_{\rm obs}/{\rm s}^{-1}$
4-MeO	10.3	370 ± 2	10.19	0.1-2.0	0.3–7.5
4-H	9.81	73 ± 1	10.0	0.05–1.5	0.07-1.5
4-H <sup>c</sup>	9.81	71 ± 1	9.6	0.5–3.0	0.17-1.1
4-Cl	9.26	52 ± 1	9.37	0.7–2.0	0.4-1.0
4-Br	9.21	44 ± 1	9.21	0.5-2.0	0.2-1.0
2-Cl, 4-Me	8.68	13.6 ± 0.2	9.40	0.7-2.0	0.1-0.3
2-Cl	8.32	$4.5 \pm 0.4$	9.20	0.7-2.0	(3–9)×10–2
4-CN	7.80	$1.28 \pm 0.01$	7.92	0.7-2.0	(1-3)×10-2
2-CN	7.22	$0.22 \pm 7 \times 10 - 3$	7.15	0.7-2.0	(2-4)×10-3
2,3,5-trifluoro	6.93	$(3.6 \pm 0.5) \times 10 - 2$	7.23	0.3–1.8	(2–7)×10–4
2,3,5-trichloro	6.58	$(5.7 \pm 0.8) \times 10 - 2$	8.03	0.3–1.5	(5–12) × 10–4
2,3,5,6-tetrafluoro <sup>d</sup>	5.41	$(8.3 \pm 2) \times 10 - 5$	6.33	10–30	$(1-3) \times 10-5$
pentafluoro <sup>d</sup>	5.33	< 4.0×10–5	5.91	10–30	1×10–5
<sup>a</sup> Measurements at 400 m <sup>b</sup> From ref. 8 and 16.	m				

<sup>c</sup>Approximately 2:1 buffer ratio [PhOH]:[PhO–].

<sup>d</sup>Measured using the sampling method.

Table 2. Kinetic data <sup>a</sup> for the reaction of <b>2</b> (b) with substituted phenoxide ions at 25 °C					
Substituents in <b>3</b>	рК <sub>а</sub> ь	$k_{\rm s}/{\rm dm}^3~{\rm mol}^{-1}~{\rm s}^{-1}$	рН	[3]/10 <sup>-2</sup> mol dm <sup>-3</sup>	$k_{\rm obs}/{\rm s}^{-1}$
4-MeO	10.3	1280 ± 20	10.04	0.1–0.5	1–8
4-H	9.81	260 ± 1	9.9	0.2–1.4	0.6-3.5
2-Cl, 4-Me	8.68	76 ± 1	9.26	0.7–2.0	0.5-1.5
2-Cl	8.32	23.5 ± 0.7	8.68	0.7–2.0	(2–5)×10–1
2-CN	7.22	$3.10 \pm 0.05$	6.92	0.7–1.7	(2–5)×10–2
2,3,5-Trichloro	6.58	$1.20 \pm 0.08$	8.22	0.3–1.5	(2–19)×10–3
2,3,5,6-Tetrafluoro	5.41	$0.015 \pm 0.001$	6.33	0.5-2.5	$(1-4) \times 10-4$
<sup>a</sup> Measurements at 400 nm <sup>b</sup> From ref. 8 and 16.	۱.				

Results for the reaction of  $\mathbf{2}(b)$  with seven ring-substituted phenoxide ions are in Table 2.

 $\beta$ rønsted plots for these reactions and for the related reactions of **2**(c) are shown in Fig. 2. For compounds **2**(a) and **2**(c), the plots show two intersecting linear correlations consistent with a two-step mechanism involving a  $\sigma$ -adduct intermediate, **4**. As predicted, the break in linearity occurs at the  $pK_a$  of the leaving group,<sup>[15]</sup> 7.12 for 4-nitrophenol and 8.19 for 3-nitrophenol. For **2**(b) the  $pK_a$  value<sup>[15]</sup> of 5.4 of the leaving group, 3,4-dinitrophenol, is below that of most of the accessible phenol nucleophiles so that a precise break in the plot is not observed.



**Figure 2.** (i) and 2(ii)  $\beta$  rønsted plots for the reaction of **2**(a), (b) and (c) with phenoxide ions. The vertical arrows correspond to the p $K_a$  values of the appropriate leaving group

Table 3. Summary of $\beta$ values					
Substrate	Nucleophile	β <sub>1</sub>	$\beta_1 + \beta_2 - \beta_{-1}$	Δβ	$-\beta_{-2}$
2(a)	Various	0.93 ± 0.08	1.88 ± 0.08	0.95	-
2(b)	Various	0.83 ± 0.06	-	-	-
2(c)	Various	0.89 ± 0.10	1.98 ± 0.06	1.09	-
Various	phenoxide	-	-	-	0.18 ± 0.03
Various	4-chlorophenoxide	-	-	-	0.21 ± 0.04

### The reverse process

It is possible to obtain additional information by measuring rate constants for reaction of single phenolic nucleophiles with a range of ring-substituted phenyl 2,4,6-trinitrophenyl ethers. Measurements were made for reaction of phenoxide ions in phenol/phenoxide buffers at constant pH with substrates **2**(a), (b),(d),(e). The wavelengths chosen were appropriate for the anionic form of the leaving group. For solubility reasons, all measurements were made in 15% (v/v) dioxan-water and with ionic strength maintained at 0.1 mol dm<sup>-3</sup>. Under first-order conditions, plots of  $k_{obs}$  versus phenoxide concentration, Fig. 3, were linear, and the slopes gave values for  $k_{-s}$ , the second-order rate constants for the reverse reaction. A second set of results was obtained for reactions with 4-chlorophenoxide ions in buffers with 4-chlorophenol.

βrønsted plots of log  $k_{-s}$  versus the  $pK_a$  values<sup>[15,17]</sup> of the leaving groups are shown in Fig. 4. As expected, straight lines, with no break, are obtained since the  $pK_a$  values associated with the nucleophiles phenol,  $pK_a$  9.81 and 4-chlorophenol,  $pK_a$  9.26 are higher than those of the leaving groups.

### **Kinetic analysis**

The results are consistent for the reaction given in Eqn (2) with (4) being treated as a steady-state intermediate. This leads to Eqn (3). The two limiting conditions corresponding to rate-limiting nucleophilic attack,  $k_2 > k_{-1}$ , and rate-limiting expulsion of the leaving group,  $k_{-1} > k_2$ , lead, respectively, to Eqns (4) and (5) with the related  $\beta$ rønsted



**Figure 3.** Variation of  $k_{obs}$  with phenoxide concentration in the reactions with **2**(a), (b), (d) and (e) in phenol/phenoxide buffers

$$k_s = \frac{k_1 \cdot k_2}{k_{-1} + k_2} \tag{3}$$

$$k_s = k_1 \tag{4}$$

$$k_s = K_1 k_2 \tag{5}$$

$$\log k_{\rm s} = \beta_1 p K_{\rm a} + C_1 \tag{6}$$

$$\log k_{\rm s} = (\beta_1 + \beta_2 - \beta_{-1}) p K_{\rm a} + C_{12} \tag{7}$$

relationships in Eqns (6) and (7). Values obtained, from Fig. 2, for the  $\beta$ rønsted exponents are in Table 3.

Ideally, for the reverse process, it would be appropriate to study reactions with the leaving groups used in the forward reaction, i.e. 4-nitrophenoxide, 3-nitrophenoxide and 3,4-dinitrophenoxide. Due to the poor reactivity of these species acting as nucleophiles, this was not possible. The approach used was to measure rate constants with the more reactive nucleophiles phenoxide and 4-chlorophenoxide. The linear plots obtained in Fig. 4 show that here the condition of Eqn (8) applies leading to the  $\beta$ rønsted relation in Eqn (9).

$$k_{-s} = k_{-2} \tag{8}$$

$$\log k_{-s} = \beta_{-2} \mathsf{p} \mathcal{K}_{\mathsf{a}} + \mathsf{C}_2 \tag{9}$$

Values for  $\beta_{-2}$ , from Fig. 4, are in Table 3. Using the information obtained, the effective charge map<sup>[14,18–20]</sup> shown in Fig. 5



**Figure 4.**  $\beta$ rønsted plots for reactions of **2**(a), (b), (d), (e) with phenoxide and 4-chlorophenoxide ions.  $pK_a$  values are for the leaving groups



Figure 5. Effective charge map for reaction of 3'-nitrophenyl-2,4,6-trinitrophenyl ether and for the associated transition states

involving displacement of the 3-nitrophenoxide ion may be constructed. Effective charge distribution for the two transition states is included. The values determined for Leffler's  $\alpha$ -parameter, Eqn (10), in this case 0.50  $\pm$  0.06, are expected to be identical for formation of an intermediate from reactant

$$\alpha = \frac{\beta_1}{\beta_{eq(1)}} = -\frac{\beta_{-2}}{\beta_{eq(2)}} \tag{10}$$

or product in a symmetrical reaction.

The significant amount of effective charge, -2.42, distributed within the trinitro-substituted moiety of the intermediate may be attributed to the strongly electron withdrawal, effect of the nitro-groups and their excellent solvation in water. For comparison, Williams and co-workers have reported an effective charge of -1.42 within the triazine ring of the intermediate 5 formed from reaction of substituted pyridines and the 1'(2,6-diphenoxy-



1,3,5-triazin-2-yl) pyridinium cation in water. Evidence for a stepwise process is confirmed by the value of  $\Delta\beta$ , 1.05 ± 0.05,

which is consistent with a substantial difference in effective charge on the reacting oxygen atoms on going from the intermediate to the transition states corresponding to the  $k_{-2}$  and  $k_2$  processes. A value of zero is expected for  $\Delta\beta$  for a concerted process.

The value of 0.85 obtained for  $\beta_1$  indicates that bond formation is well advanced in the transition state for formation of the intermediate. That this value is higher than those, 0.5–0.7, normally associated<sup>[2]</sup> with nucleophilic substitutions may beattributed to the strongly electron-withdrawing effect of the trinitrobenzene ring. Values of  $\beta$  close to or higher than one have been attributed to the intervention of an SET pathway<sup>[21,22]</sup> for substitution but there is no evidence that this applies here.

### **EXPERIMENTAL**

Phenyl 2,4,6-trinitrophenyl ethers 2(a)–(e) were prepared by the reaction of picryl chloride with the appropriate phenoxide in water. The relevant phenol (0.013 mol. equiv) with sodium hydroxide (0.01 mol, 0.4 g) in water (15 cm<sup>3</sup>) was stirred for 15 min to give a solution after which picryl chloride (0.008 mol, 2 g) was gradually added over 30 min. The mixture was stirred and heated at 45 °C for 8 h, or in the case of 2(b) for 24 h. After cooling, a further 30 cm<sup>3</sup> of water was added to dissolve any remaining sodium chloride or picric acid impurities. The precipitate produced was separated by filtration, washed with ethanol and recrystallised from ethanol. 1H NMR data, measured with a Varian Gemini 400 instrument, and melting points are in Table 4.

Table 4. Data for phenyl 2,4,6-trinitrophenyl ethers				
Compound	m.p.	lit m.p.	1H NMR results in DMSO-d <sub>6</sub>	
<b>2</b> (a)	163	157 <sup>[23]</sup>	9.32(s) 8.30(d, J=9.0 Hz)	
•(1)	202	202[24]	7.35(d, J = 9.0 Hz)	
<b>2</b> (b)	203	202	9.3/(s) 8.40(d, $J = 9.1 Hz)$	
			8.0/(0, J = 2.9 HZ)	
	170	174[25]	7.70(uu, J = 9.1 and 2.9 Hz)	
<b>Z</b> (C)	172	174	9.29(S) 8.05(dd, J = 8.4 and 3.0 Hz)	
			7.90(l, J = 3.0 HZ)	
			7.7 I(L, $J = 0.4 \Pi Z$ )	
<b>2</b> (d)	107	120[26]	7.02(00, J = 6.4  and  5.0  Hz)	
<b>Z</b> (U)	127	128	9.29(5) 9.94(5)	
			$7.34(u, J = 0.0 \Pi Z)$	
<b>7</b> (a)	65		$7.50(d, J = 0.0 \Pi Z)$	
<b>Z</b> (e)	co		9.28(5) 9.95(5)	
			7.74(0, J = 7.8 Hz)	
			7.64(t, J = 7.8 Hz)	
			7.50(m)	

Phenols were the purest available commercial specimens. Buffer solutions were prepared by addition of measured quantities of carbonate free sodium hydroxide solution to the appropriate phenol. pH values were measured using a Jenway 3020 pH meter (accurate to 0.02 pH units). UV/visible spectra were measured using Shimadzu UV-2101 PC or Perkin-Elmer Lambda 2/12 instruments, which were also used for kinetic measurements. For the faster reactions, either an Applied Photophysics SX-17 MV or a Hi-Tech SF-3 stopped-flow spectrometer was used.

Kinetic measurements were made by following the appearance of the appropriate leaving group in its anionic form. For phenols with very low reactivity, such as tetra- or penta-halogenated phenols, measurements were made at pH values lower than the  $pK_a$  value of the leaving group. Here, a sampling technique was used where 1 cm<sup>3</sup> of reaction solution was removed and added to 1 cm<sup>3</sup> of sodium carbonate solution in a cuvette. Absorbances were measured immediately, before further reaction could occur. This technique restores the pH to a value above that of the  $pK_a$  of the leaving group ensuring conversion to the anionic form. These reactions were typically followed over several days.

All measurements were made at 25° and with ionic strength maintained at 0.1 mol  $\rm dm^{-3}$  with sodium chloride.

### **Reactions with hydroxide ions**

In order to confirm that interferences from reaction of substrates with hydroxide ions were minimal, rate constants were measured for the direct reaction of 2(a) and 2(b) with sodium hydroxide in water. For 2 (a), the UV/visible spectra of the products showed a maximum at 396 nm and were consistent with the formation of picrate ions and 4-nitrophenoxide. There was no evidence for the formation of intermediates in spectroscopically observable concentrations. Nor was there evidence, at the low hydroxide concentration  $(1-5 \times 10^{-3} \text{ mol dm}^{-3})$ used, for hydroxide attack at the 3-position which has been observed in related systems.<sup>[27]</sup> Hence, the reaction is interpreted as rate-determining nucleophilic attack by hydroxide. First-order rate constants,  $k_{obs}$ , were measured with [OH–] >> [2a] or [2b] and were found to increase linearly with hydroxide concentrations. Values obtained for the second-order rate constant,  $k_{OH}$ , were 3.5 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for **2**(a) in 5% (v/v) dioxan-water and 3.9 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for 2(b) in 15% (v/v) dioxan-water. These values indicate that at the very low hydroxide concentrations present in the phenol/phenoxide buffers, reactions with hydroxide will not interfere significantly.

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