

Kinetics and Mechanism of the Aminolysis of 4-Methylphenyl and 4-Chlorophenyl 2,4-Dinitrophenyl Carbonates in Aqueous Ethanol

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The reactions of anilines with 4-methylphenyl and 4-chlorophenyl 2,4-dinitrophenyl carbonates (MPDNPC and CIPDNPC, respectively) and the latter substrate with secondary alicyclic (SA) amines are subjected to a kinetic study in 44 wt % ethanol–water solution, at 25.0 °C, and an ionic strength of 0.2 M (KCl). The reactions are studied by following spectrophotometrically (360 nm) the release of 2,4-dinitrophenoxide anion. Under amine excess, pseudo-first-order rate coefficients (k_{obsd}) are found. Plots of k_{obsd} vs [amine] are linear and pH-independent, with slope k_{N} . The Brønsted-type plots ($\log k_{\text{N}}$ vs $\text{p}K_{\text{a}}$ of aminium ions) are linear, with slopes $\beta = 0.68$ and 0.66 for the reactions of anilines with MPDNPC and CIPDNPC, respectively, and $\beta = 0.44$ for the reactions of SA amines with CIPDNPC. The magnitude of the slope for the latter reaction indicates that its mechanism is concerted. The slope values for the reactions of anilines are in the borderline between stepwise and concerted mechanisms. The sensitivity of $\log k_{\text{N}}$ to the basicity of the nonleaving group (β_{nlg}) is ca. -0.7 for the reactions of anilines, in agreement with that found for the SA reactions (β_{nlg} ca. -0.6). These results suggest that the reactions of anilines are concerted, although it is also possible that both mechanisms (stepwise and concerted) operate simultaneously. By comparison of the reactions under investigation between them and with similar aminolyses, the following conclusions can be drawn: (i) CIPDNPC is more reactive than MPDNPC toward the two amine series. (ii) The change of water to aqueous ethanol destabilizes a zwitterionic tetrahedral intermediate. (iii) The change of the nonleaving group from MeO to 4-methylphenoxy or 4-chlorophenoxy also destabilizes this intermediate.

Introduction

Although there have been many reports on the kinetics and mechanisms of the aminolyses (several types of amines) of alkyl aryl carbonates and their mechanisms have been clarified,^{1,2} there have been only a few investigations concerning the kinetics of the aminolyses of diaryl carbonates.^{3,4} The latter studies involve the reactions of several nitro- and dinitrophenyl phenyl carbonates with quinuclidines in water,³ the reactions of 4-methylphenyl 4-nitrophenyl and 4-methylphenyl 2,4-dinitrophenyl carbonates (MPNPC and MPDNPC, respectively) with secondary alicyclic (SA) amines in aqueous

ethanol,^{4a} the reactions of the latter amines with phenyl 2,4-dinitrophenyl carbonate (PDNPC) in water,^{4b} and the reactions of quinuclidines with MPNPC and 4-chlorophenyl 4-nitrophenyl carbonate (CIPNPC), and the latter compound with SA amines in aqueous ethanol.^{4c}

The quinuclidinolysis of PDNPC in water was claimed to be stepwise, through the formation of a zwitterionic tetrahedral intermediate (T^{\pm}), on the basis of the slightly curved Brønsted-type plot obtained.³ This plot was explained by a change in the rate-determining step, from breakdown of T^{\pm} to its formation, with the increasing basicity of the amine.³ Nevertheless, this mechanism has been questioned in the light of the linear Brønsted-type plot of slope (β) 0.4 obtained for the aminolysis (SA) of PDNPC in water, which indicates a concerted process.^{4b}

The reactions of SA amines with MPNPC in aqueous ethanol exhibit a biphasic Brønsted-type plot with slopes $\beta_1 = 0.2$ (high $\text{p}K_{\text{a}}$ region) and $\beta_2 = 0.9$ (low $\text{p}K_{\text{a}}$ region), which was attributed to a stepwise mechanism through a T^{\pm} intermediate and a change in the rate-limiting step with amine basicity.^{4a} On the other hand, the reactions of the latter amines with MPDNPC in aqueous ethanol were claimed to be concerted (single step without T^{\pm}) on the basis of the slightly curved Brønsted plot found.^{4a}

The quinuclidinolysis of MPNPC and CIPNPC exhibit linear Brønsted plots of slopes (β) ca. 0.9, consistent with stepwise mechanisms with rate-determining breakdown

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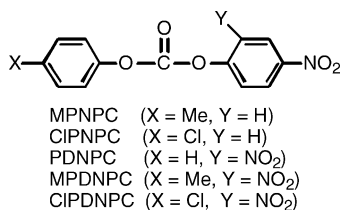
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of T[±] to products.^{4c} The reaction of the latter substrate with SA amines shows a biphasic Brønsted plot with slopes $\beta_1 = 0.2$ (high pK_a region) and $\beta_2 = 0.9$ (low pK_a region), consistent with a stepwise mechanism through an intermediate T[±].^{4c}

To extend our kinetic studies on the aminolysis of diaryl carbonates and with the aim to shed some light on these mechanisms, in the present work we investigate the reactions of a series of anilines with MPDNPC and CIPDNPC and that of the latter substrate with a series of SA amines in aqueous ethanol. A specific objective is to assess the influence of the nonleaving group, the amine nature, and the solvent on the kinetics and mechanisms of these reactions. This will be achieved by a kinetic comparison of the title reactions between them and with similar aminolyses in aqueous ethanol and in water.



Experimental Section

Materials. The anilines⁵ and SA amines⁶ were purified either by distillation or recrystallization. MPDNPC was prepared as described.^{4a} CIPDNPC was obtained by a modification of a standard procedure,³ as previously reported.⁷ 4-Methylphenyl and 4-chlorophenyl *N*-phenyl carbamates (ArO-CO-NH-Ph) and 1-(4-chlorophenoxy carbonyl)morpholine (4-ClC₆H₄O-CO-NC₄H₈O), which are the products of the reactions of the two substrates with aniline and CIPDNPC with morpholine, were prepared by a variation of a standard synthesis,⁸ as published for ethyl phenyl carbamate,⁹ from the corresponding chloroformates and aniline in acetonitrile. The crystallized (ethanol) 4-methylphenyl and 4-chlorophenyl *N*-phenyl carbamates melted at 111–112 °C (lit.¹⁰ mp 108–110 °C) and 146–147 °C (lit.¹⁰ mp 148–150 °C), respectively. 1-(4-Chlorophenoxy carbonyl)morpholine melted at 76.8–77.3 °C (lit.¹¹ mp 80.0 °C). These products were identified by ¹H NMR (200 MHz, CDCl₃) and IR analyses.

Determination of pK_a. The pK_a values of the conjugate acids of the anilines were determined spectrophotometrically in 44 wt % ethanol–water solution, 25.0 °C, ionic strength 0.2 (KCl), as reported.¹²

Kinetic Measurements. These were carried out by means of a diode array spectrophotometer in 44 wt % ethanol–water solution, at 25.0 ± 0.1 °C, ionic strength 0.2 M (KCl). The reactions were followed at 360 nm (formation of 2,4-dinitrophenoxide anion).

All reactions were studied under excess of the amine over the substrate. The initial substrate concentration was 5 × 10⁻⁵

TABLE 1. Experimental Conditions and *k*_{obsd} Values for Reactions of Secondary Alicyclic Amines with 4-Chlorophenyl 2,4-Dinitrophenyl Carbonate (CIPDNPC)^a

| amine | pH | 10 ³ [N] _{tot} ^b (M) | 10 ³ <i>k</i> _{obsd} (s ⁻¹) | no. of runs |
|--|------------------|---|---|-------------|
| piperidine | 6.7 ^c | 0.427–3.00 | 0.265–0.375 | 7 |
| | 7.0 ^c | 0.853–3.00 | 0.315–0.466 | 6 |
| | 7.3 ^c | 1.28–3.41 | 0.398–0.781 | 6 |
| piperazine | 9.41 | 0.824–2.40 | 53.2–219 | 6 |
| | 9.71 | 0.843–2.40 | 83.0–324 | 6 |
| | 10.01 | 0.411–2.88 | 49.0–449 | 7 |
| 1-(2-hydroxyethyl)-piperazine | 8.79 | 0.416–2.91 | 4.59–35.1 | 7 |
| | 9.09 | 0.416–2.91 | 9.69–54.7 | 7 |
| | 9.39 | 0.416–2.50 | 13.0–59.8 | 6 |
| morpholine | 8.18 | 0.20–2.40 | 8.50–76.0 | 7 |
| | 8.48 | 0.20–2.40 | 7.10–99.6 | 7 |
| | 8.78 | 0.20–2.00 | 14.0–105 | 6 |
| 1-formylpiperazine | 7.33 | 0.20–2.40 | 3.00–20.0 | 7 |
| | 7.63 | 0.20–2.40 | 7.00–27.0 | 6 |
| | 7.93 | 0.20–2.40 | 8.00–36.0 | 6 |
| piperazinium ion | 5.07 | 0.42–3.00 | 0.686–3.86 | 7 |
| | 5.37 | 0.40–2.40 | 0.944–4.69 | 6 |
| | 5.67 | 0.45–3.16 | 0.965–6.12 | 7 |
| 1-(2-hydroxyethyl)-piperazinium ion ^d | 4.30 | 8.76–30.7 | 0.896–2.72 | 6 |
| | 4.60 | 8.92–31.2 | 1.09–3.13 | 6 |
| | 4.90 | 9.11–31.5 | 1.36–3.76 | 6 |

^a In 44 wt % ethanol–water, at 25.0 °C, ionic strength 0.2 (KCl).

^b Concentration of total amine (free base plus protonated forms).

^c In the presence of phosphate buffer 0.01 M. ^d The pK_a of the conjugate acid of this reactive species is 5.6; buffer is due to partial ionization of the dication.

M. In the reactions of both substrates with anilines and in the reaction of CIPDNPC with piperidine, phosphate buffer 0.01M was used. In the other reactions the pH was maintained by partial protonation of the SA amines.

Pseudo-first-order rate coefficients (*k*_{obsd}) were found for all reactions; these were determined by means of the spectrophotometer kinetic software for first-order reactions. The experimental conditions of the reactions and the *k*_{obsd} values are shown in Tables 1–3.

Product Studies. For the present reactions one of the products was identified as 2,4-dinitrophenoxide anion; this was achieved by comparison of the UV–vis spectra after completion of the reactions with an authentic sample of 2,4-dinitrophenol 5 × 10⁻⁵ M, under the same conditions. For the reactions of MPDNPC and CIPDNPC with aniline and the latter substrate with morpholine, the other product was identified as 4-methylphenyl and 4-chlorophenyl *N*-phenyl carbamates and 1-(4-chlorophenoxy carbonyl)morpholine, respectively. This was concluded by comparison of a sample at the end of the reactions with an authentic sample of the corresponding product, by HPLC with column Eurospher C-18 (10 cm, 7μm), eluant acetonitrile/water = 70/30, isocratic mode 0.5 mL/min.

Results and Discussion

The kinetic law obtained under the reaction conditions is that described by eq 1, where P is 2,4-dinitrophenoxide anion, S is the substrate, and *k*_{obsd} is the pseudo-first-order rate coefficient (excess of amine was used throughout).

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

Plots of *k*_{obsd} against [amine] at constant pH were linear in accordance with eq 2, where *k*₀ and *k*_N are the rate

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TABLE 2. Experimental Conditions and k_{obsd} Values for Reactions of Anilines with 4-Chlorophenyl 2,4-Dinitrophenyl Carbonate (CIPDNPC)^a

| amine | pH ^b | 10 ³ [N] _{tot} ^c (M) | 10 ³ k_{obsd} (s ⁻¹) | no. of runs |
|---------------------|-----------------|--|---|----------------|
| 4-methoxyaniline | 7.0 | 1.25–15.0 | 2.63–26.8 | 7 |
| | 7.2 | 0.625–12.5 | 1.44–22.1 | 6 |
| | 7.5 | 0.625–12.5 | 1.46–23.1 | 6 |
| 4-methylaniline | 7.0 | 0.65–12.5 | 0.633–7.42 | 7 |
| | 7.2 | 0.65–12.5 | 0.752–8.42 | 7 |
| | 7.5 | 0.65–12.5 | 0.724–8.25 | 7 |
| aniline | 7.0 | 5.0–60.0 | 2.23–22.9 | 7 |
| | 7.2 | 5.0–60.0 | 2.16–20.9 | 7 |
| | 7.5 | 5.0–60.0 | 2.24–22.7 | 6 |
| 3-methoxyaniline | 7.0 | 0.50–60.0 | 0.389–1.48 | 7 |
| | 7.2 | 0.50–16.0 | 0.370–3.69 | 6 |
| | 7.5 | 1.00–12.0 | 0.451–2.67 | 6 |
| 3-aminoacetophenone | 7.0 | 2.50–30.0 | 0.439–2.17 | 6 |
| | 7.2 | 2.50–30.0 | 0.507–2.57 | 7 |
| | 7.5 | 2.50–25.0 | 0.438–1.76 | 6 |
| 3-aminobenzonitrile | 7.0 | 6.50–100 | 0.324–1.18 | 8 |
| | 7.2 | 6.50–78.0 | 0.342–1.05 | 7 |
| | 7.5 | 6.50–78.0 | 0.355–0.962 | 6 |
| 4-aminoacetophenone | 7.0 | 1.10–17.6 | 0.264–0.371 | 9 |
| | 7.2 | 2.20–52.0 | 0.254–0.567 | 7 |
| | 7.5 | 6.50–78.0 | 0.296–0.741 | 7 |

^a In 44 wt % ethanol–water, at 25.0 °C and an ionic strength of 0.2 (KCl). ^b pH maintained with phosphate buffer 0.01 M. ^c Concentration of total amine (free base plus protonated forms).

TABLE 3. Experimental Conditions and k_{obsd} Values for Reactions of Anilines with 4-Methylphenyl 2,4-Dinitrophenyl Carbonate (MPDNPC)^a

| amine | pH ^b | 10 ³ [N] _{tot} ^c (M) | 10 ³ k_{obsd} (s ⁻¹) | no. of runs |
|---------------------|-----------------|--|---|----------------|
| 4-methoxyaniline | 7.0 | 1.25–15.0 | 0.820–8.92 | 6 |
| | 7.2 | 1.25–15.0 | 0.774–8.08 | 7 |
| | 7.5 | 1.25–15.0 | 0.831–8.33 | 7 |
| 4-methylaniline | 7.0 | 0.65–12.5 | 0.288–3.00 | 7 |
| | 7.2 | 0.65–12.5 | 0.248–3.06 | 7 |
| | 7.5 | 0.65–12.5 | 0.244–3.35 | 7 |
| aniline | 7.0 | 5.00–60.0 | 0.675–6.57 | 7 |
| | 7.2 | 5.00–60.0 | 0.681–6.64 | 7 |
| | 7.5 | 5.00–60.0 | 0.780–7.13 | 7 |
| 3-methoxyaniline | 7.0 | 1.00–16.0 | 0.148–1.23 | 7 |
| | 7.2 | 1.00–16.0 | 0.149–1.23 | 7 |
| | 7.5 | 1.00–16.0 | 0.150–1.21 | 7 |
| 3-aminoacetophenone | 7.0 | 2.50–30.0 | 0.184–0.787 | 6 |
| | 7.2 | 1.25–25.0 | 0.104–0.587 | 6 |
| | 7.5 | 2.50–30.0 | 0.175–0.838 | 7 |
| 3-aminobenzonitrile | 7.0 | 6.50–100 | 0.106–0.424 | 7 |
| | 7.2 | 6.50–100 | 0.109–0.431 | 7 |
| | 7.5 | 6.50–100 | 0.0987–0.351 | 7 |
| 4-aminoacetophenone | 7.0 | 13.0–78.0 | 0.0865–0.199 | 6 |
| | 7.2 | 6.50–78.0 | 0.0846–0.190 | 7 |
| | 7.5 | 6.50–78.0 | 0.0867–0.198 | 7 |

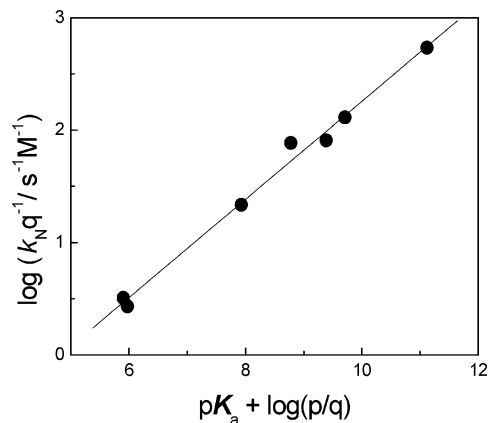
^a In 44 wt % ethanol–water, at 25.0 °C and an ionic strength of 0.2 (KCl). ^b pH maintained with phosphate buffer 0.01 M. ^c Concentration of total amine (free base plus protonated forms).

coefficients for solvolysis and aminolysis of the substrates, respectively. The values of k_0 and k_N were obtained as the intercept and slope, respectively, of plots of k_{obsd} against [amine]. These values were pH independent, within the pH range employed for the reactions of each amine. For the solvolysis of MPDNPC and CIPDNPC in the 7.0–7.5 pH range, the values of k_0 are 8×10^{-5} and $2.8 \times 10^{-4} \text{ s}^{-1}$, respectively. For the solvolysis of CIPDNPC, the k_0 (s⁻¹) values at other pH are 1×10^{-3} (pH 9–10), 6×10^{-4} (pH 8.2–8.8), 6×10^{-5} (pH 5.1–

TABLE 4. Values of pK_a for Conjugate Acids of Secondary Alicyclic Amines and k_N Values for Reactions of These Amines with 4-Chlorophenyl 2,4-Dinitrophenyl Carbonate (CIPDNPC)^a

| amine | pK_a | k_N (s ⁻¹ M ⁻¹) |
|------------------------------------|--------|--|
| piperidine | 10.82 | 541 ± 13 |
| piperazine | 9.71 | 259 ± 8 |
| 1-(2-hydroxyethyl)piperazine | 9.09 | 81 ± 3 |
| morpholine | 8.48 | 77 ± 3 |
| 1-formylpiperazine | 7.63 | 21.6 ± 0.8 |
| 1-(2-hydroxyethyl)piperazinium ion | 5.60 | 3.2 ± 0.1 |
| piperazinium ion | 5.37 | 2.7 ± 0.1 |

^a Both the pK_a and k_N values were determined in 44 wt % aqueous ethanol, at 25.0 °C, ionic strength 0.2 (KCl).

**FIGURE 1.** Brønsted-type plot (statistically corrected) obtained in the reactions of SA amines with 4-chlorophenyl 2,4-dinitrophenyl carbonate (CIPDNPC) in 44 wt % ethanol–water, at 25.0 °C and an ionic strength of 0.2 M. The slope (β) is 0.44.

5.7), and 3×10^{-5} (pH 4.3–4.9).

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

For the reactions of SA amines with CIPDNPC the values of k_N (obtained as the slopes of plots of eq 2) and pK_a are summarized in Table 4. These values, as well as those of the pK_a of the conjugate acids of the SA amines, were statistically corrected with $q = 2$ for piperazine and $p = 2$ for the conjugate acids of the SA amines, except that for piperazinium ion with $p = 4$.^{1f,4–6,13} With these corrected values the Brønsted-type plot (shown in Figure 1) was obtained. The slope of this linear plot is $\beta = 0.44$.

The values of k_N (obtained as the slopes of plots of eq 2) for the reactions of anilines with MPDNPC and CIPDNPC are shown in Table 5, together with the experimentally determined pK_a values of the anilinium ions. With these k_N values and those of the statistically corrected pK_a of the conjugate acids of the anilines (with $q = 1$ and $p = 3$),^{5,9,13} the Brønsted-type plots (shown in Figure 2) were obtained. These linear plots show slopes $\beta = 0.68$ and 0.66, respectively.

The value of $\beta = 0.44$ found for the reactions of SA amines with CIPDNPC (Figure 1) is in accord with a concerted process where the structure of the transition state remains constant with the variation of the nucleo-

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TABLE 5. Values of pK_a for Conjugate Acids of Anilines and k_N Values for Reactions of These Amines with 4-Methylphenyl 2,4-Dinitrophenyl Carbonate (MPDNPC) and 4-Chlorophenyl 2,4-Dinitrophenyl Carbonate (CIPDNPC)^a

| amine | pK_a | $10^2 k_N$ ($s^{-1} M^{-1}$) | |
|---------------------|--------|--------------------------------|------------------|
| | | MPDNPC | CIPDNPC |
| 4-methoxyaniline | 5.29 | 55 ± 1 | 175 ± 2 |
| 4-methylaniline | 4.90 | 24.4 ± 0.6 | 61 ± 1 |
| aniline | 4.46 | 11.1 ± 0.2 | 36 ± 1 |
| 3-methoxyaniline | 4.26 | 7.2 ± 0.03 | 20.9 ± 0.2 |
| 3-aminoacetophenone | 3.10 | 2.3 ± 0.1 | 6.7 ± 0.3 |
| 3-aminobenzonitrile | 2.12 | 0.35 ± 0.01 | 0.93 ± 0.002 |
| 4-aminoacetophenone | 1.73 | 0.149 ± 0.006 | 0.62 ± 0.01 |

^a Both the pK_a and k_N values were determined in 44 wt % aqueous ethanol, at 25.0 °C and an ionic strength of 0.2 (KCl)

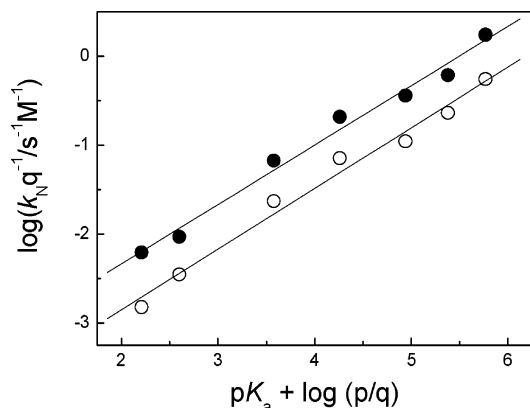


FIGURE 2. Brønsted-type plots (statistically corrected) obtained in the reactions of anilines with CIPDNPC (●) and MPDNPC (○) in 44 wt % ethanol–water, at 25.0 °C and an ionic strength of 0.2 M. The slopes (β) are 0.68 and 0.66, respectively.

phile basicity. This β value is in agreement with those found in the following concerted reactions in water: SA amines with *S*-(2,4-dinitrophenyl) and *S*-(2,4,6-trinitrophenyl) *O*-ethyl thiocarbonates ($\beta = 0.56$ and 0.48 , respectively),¹⁴ quinuclidines with these two substrates ($\beta = 0.54$ and 0.47 , respectively),¹⁵ anilines with the latter compound ($\beta = 0.54$),⁹ and SA amines with 2,4,6-trinitrophenyl acetate and 2,4,6-trinitrophenyl methyl carbonate ($\beta = 0.41$ and 0.36 , respectively).^{1f}

For the reactions of SA amines with MPDNPC in 44 wt % ethanol–water a slightly curved Brønsted-type plot was found, which was explained by a concerted mechanism.^{4a} If 4-Me as substituent in the nonleaving group of this carbonate yields a concerted process, it is reasonable that the substitution of this group by 4-Cl should also lead to a concerted mechanism. This is because the latter substituent, being more electron-withdrawing than Me, should destabilize even more the hypothetical tetrahedral intermediate (in a hypothetical stepwise process) compared to that with 4-Me.

The k_N values found for the reactions of SA amines with CIPDNPC in 44 wt % ethanol–water (Table 4) are

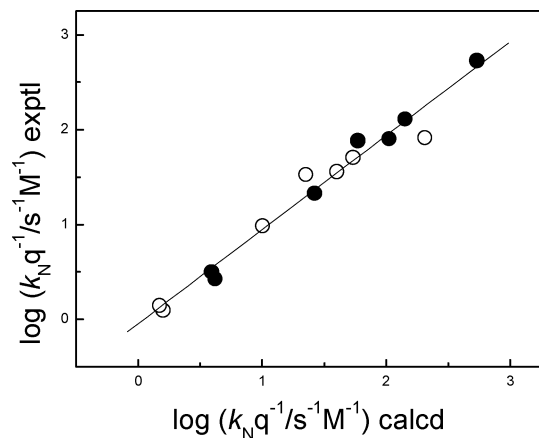


FIGURE 3. Logarithmic plot of experimental k_N/q vs calculated k_N/q (through eq 3) for the reactions of SA amines with CIPDNPC (●, this work) and MPDNPC (○, ref 4a) in 44 wt % ethanol–water, at 25.0 °C and an ionic strength of 0.2 (KCl).

larger than those obtained in the same aminolysis of MPDNPC in the same solvent.^{4a} This can be explained by the stronger electron withdrawal from 4-Cl in CIPDNPC than 4-Me in MPDNPC, which leaves the former carbonate more prone to nucleophilic attack by the amine.¹⁶

With the k_N values (statistically corrected) found in the reactions of SA amines with CIPDNPC, together with those for the same aminolysis of MPDNPC,^{4a} and the pK_a values of both the nucleophiles (statistically corrected) and the nonleaving groups (10.1 and 9.4 for 4-methylphenol and 4-chlorophenol in water, respectively), eq 3 can be deduced by regression analysis ($n = 14$, $R^2 = 0.976$). In this expression N, and nlg refer to the nucleophile and the nonleaving group, respectively; the pK_a coefficients (β) are subjected to an error of ± 0.1 .

$$\log\left(\frac{k_N}{q}\right) = 3.81 + 0.41pK_a(N)_{\text{corr}} - 0.6pK_a(\text{nlg}) \quad (3)$$

Figure 3 shows a plot of experimental $\log(k_N/q)$ against calculated $\log(k_N/q)$ (through eq 3). The slope is unity, and the intercept is zero.

The greater reactivity of CIPDNPC compared with that of MPDNPC is a result of the negative value of β_{nlg} (-0.6) and the larger value of the pK_a of 4-methylphenol compared with that of 4-chlorophenol (10.1 and 9.4 in water, respectively).

For the reactions of anilines with MPDNPC and CIPDNPC the magnitude of the Brønsted slopes, $\beta = 0.68$ and 0.66 , respectively (Figure 2), are near the lower limit of the Brønsted slopes found in stepwise aminolyses of similar substrates when the breakdown to products of the zwitterionic tetrahedral intermediate (T^\pm) is the rate-determining step.^{17,18} For instance, Brønsted slopes of 0.7 have been found in the stepwise reactions of SA amines with phenyl and 4-chlorophenyl ethyl thiocarbonates in water.¹⁷ Similarly, Brønsted slope values of 0.8 or lower

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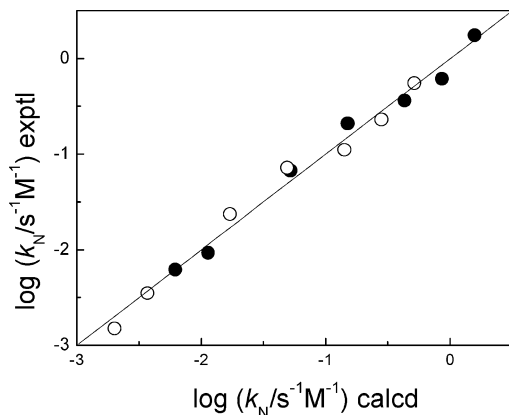


FIGURE 4. Logarithmic plot of experimental k_N vs calculated k_N (through eq 4) for the reactions of a series of anilines with CIPDNPC (●) and MPDNPC (○), in 44 wt % ethanol–water solution, 25.0 °C, ionic strength 0.2 (KCl).

have been reported for the stepwise aminolysis of 2,4-dinitrophenyl acetate and 1-acetoxy-4-methoxy-pyridinium ion.¹⁸

On the other hand, linear Brønsted plots with slope values of ca. 0.6 have been found for the concerted reactions of pyridines with *N*-methoxycarbonylisoquinolinium ion¹⁹ and SA amines with ethyl 2,4-dinitrophenyl thiolcarbonate.^{14a} Furthermore, linear Brønsted plots with slopes greater than 0.6 have been obtained for the concerted phenolyses of 4-chloro-2-nitrophenyl acetate ($\beta = 0.64$),²⁰ 3-nitrophenyl formate ($\beta = 0.64$),²¹ 3-nitrophenyl acetate ($\beta = 0.66$),²¹ 4-nitrophenyl and 4-formylphenyl acetates ($\beta = 0.75$ and 0.79 , respectively),²⁰ and CIPNPC ($\beta = 0.67$).^{7b}

Therefore, judging only by the magnitudes of the Brønsted slopes ($\beta = 0.66$ – 0.68) found for the reactions of anilines with MPDNPC and CIPDNPC it is very difficult to decide which is the mechanism (stepwise or concerted) of these reactions. Nevertheless, the following discussion allows us to be more inclined to the concerted process.

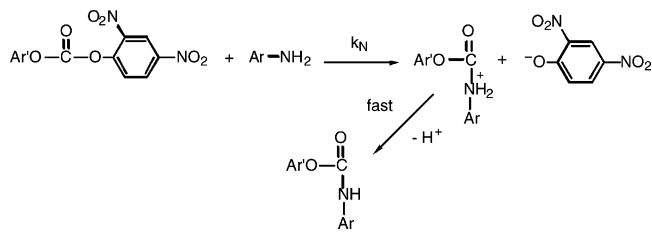
With the k_N values found in the present reactions of anilines, together with the pK_a values of the conjugate acids of the nucleophiles (statistically corrected) and nonleaving groups (the latter pK_a are 10.1 and 9.4 for 4-methylphenol and 4-chlorophenol in water, respectively), eq 4 can be deduced by regression analysis ($n = 14$, $R^2 = 0.986$). In this expression N and nlg refer to the nucleophile and the nonleaving group, respectively; the pK_a coefficients (β) are subjected to an error of ± 0.1 .

$$\log k_N = 2.82 + 0.68pK_a(N)_{\text{corr}} - 0.69pK_a(\text{nlg}) \quad (4)$$

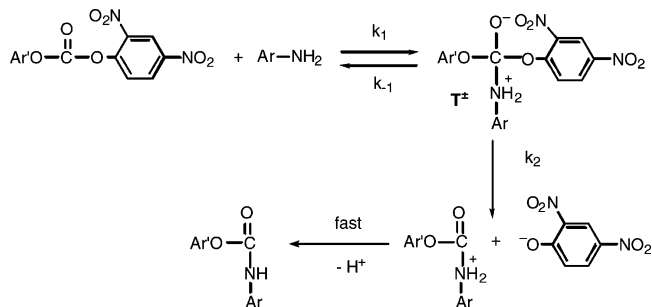
A logarithmic plot of the experimental k_N vs the calculated one through eq 4 is shown in Figure 4; the slope is unity and the intercept is zero.

For the reactions of anilines the sensitivity of $\log k_N$ to the nonleaving group basicity (β_{nlg} ca. -0.7 in eq 4) is similar to that shown by the reactions of SA amines with

SCHEME 1



SCHEME 2



the same substrates ($\beta_{\text{nlg}} = -0.6$ in eq 3), which suggests that both reaction series are ruled by the same (concerted) mechanism. This contrasts with the β_{nlg} values exhibited by the SA aminolysis and quinuclidinolysis of MPNPC and CIPNPC ($\beta_{\text{nlg}} = -0.3$ and -0.2 , respectively), which were shown to be stepwise reactions where the breakdown of the zwitterionic tetrahedral intermediate (T^\pm) to products is the rate-determining step.^{4c}

Therefore, the mechanism that we propose for the reactions of anilines with MPDNPC and CIPDNPC is shown in Scheme 1, where Ar' is a substituted phenyl group (4-chlorophenyl or 4-methylphenyl) and Ar-NH₂ is a substituted aniline. Nevertheless, in view of the borderline β_N values shown by these reactions it is also possible that the mechanism is stepwise, through a T^\pm intermediate, with rate-limiting decomposition of T^\pm to products (Scheme 2). It is also possible that both mechanisms occur simultaneously if the transition states involved are energetically similar.

As seen in Figure 2, CIPDNPC is more reactive (larger k_N values) than the methyl derivative toward anilines. This is reasonable taking into account that 4-Cl is more electron withdrawing than 4-Me.

A plot (not shown) of $\log k_N$ for the anilinolysis of CIPDNPC against $\log k_N$ for the same aminolysis of MPDNPC is linear, according to eq 5 ($n = 7$; $R^2 = 0.995$). This equation shows that the reactivity of CIPDNPC is ca. 2.8-fold greater than that of MPDNPC toward a given amine.

$$\log k_N(\text{CIPDNPC}) = 0.98 \log k_N(\text{MPDNPC}) + 0.45 \quad (5)$$

It has been found that the reactions of anilines with ethyl *S*-(2,4-dinitrophenyl) thiolcarbonates in water are stepwise⁹ whereas those of SA amines with the same substrate in the same solvent are concerted.^{14a} This means that the zwitterionic tetrahedral intermediate formed with a given aniline is greatly destabilized by substitution of this amine by an isobasic SA amine. This has been attributed to the superior leaving ability of SA

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amines from a (hypothetical) intermediate compared with isobasic anilines.⁹

If the reactions of MPDNPC and CIPDNPC with anilines are concerted, as are those of these carbonates with SA amines,^{4a} this means that the substitution of a SA amino group in a hypothetical tetrahedral intermediate by an isobasic anilino group does not bring enough stabilization to the hypothetical intermediate as to change the mechanism from concerted to stepwise. It is possible that for the reactions of SA amines the mechanism is enforced concerted (the "intermediate" is too unstable to exist) and for the reactions of anilines the intermediate does exist but is so unstable that the concerted path is favored as the result of a smaller free energy of activation compared to the stepwise process.²²

The reactions of anilines with methyl 2,4-dinitrophenyl carbonate in water are stepwise.^{1e} If the reactions of the same amines with MPDNPC and CIPDNPC in aqueous ethanol are concerted (this work), it means that the change of both the solvent (from water to aqueous ethanol) and the nonleaving group (from MeO to ArO) destabilize the zwitterionic tetrahedral intermediate. The following precedents support this conclusion.

The reactions of SA amines with *O*-ethyl *S*-(2,4,6-trinitrophenyl) dithiocarbonate in water are driven by a stepwise mechanism,^{23a} in contrast to the same reactions in aqueous ethanol, which are concerted.^{23b} These results

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indicate that the latter solvent destabilizes the tetrahedral intermediate that is formed in the reactions in water. On the other hand, the aminolysis (SA) of ethyl 4-nitrophenyl thionocarbonate in water is stepwise,^{24a} whereas the same aminolysis of bis(4-nitrophenyl) thionocarbonate in water is concerted.^{24b} This indicates that the change of EtO to 4-nitrophenoxy destabilizes the tetrahedral intermediate to the point of a mechanistic change.

Therefore, according to the above results, the change in mechanism from stepwise for the reactions of anilines with methyl 2,4-dinitrophenyl carbonate in water^{1e} to concerted for those of the same amines with MPDNPC and CIPDNPC in aqueous ethanol (this work) should be due to the destabilization caused to the tetrahedral intermediate by the change of both the solvent (from water to aqueous ethanol) and the nonleaving group (from MeO to ArO).

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