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Kinetics and Mechanism of the Anilinolysis of Aryl 4-Nitrophenyl Carbonates in Aqueous Ethanol

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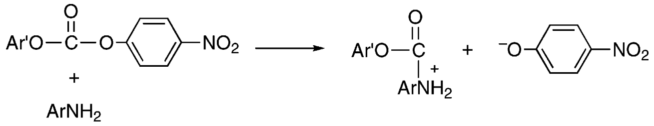

For Ar' = 4-methylphenyl and 4-chlorophenyl the reactions are stepwise
For Ar' = 4-nitrophenyl the reaction is concerted

The reactions of anilines with 4-nitrophenyl, 4-methylphenyl, and 4-chlorophenyl 4-nitrophenyl carbonates (BNPC, MPNPC and ClPNPC, respectively) are studied kinetically in 44 wt % ethanol−water, at 25.0 °C, with an ionic strength of 0.2 M (KCl). Plots of k_{obsd} vs [amine] are linear, with the slopes (k_N) independent of pH. The Brønsted-type plots (log k_N vs pK_a of conjugate acids of anilines) are linear, with slopes $\beta = 0.65$, 0.85, and 0.78 for the reactions of anilines with BNPC, MPNPC, and ClPNPC, respectively. The values of the slopes for the two latter reactions are in accordance with those obtained in stepwise mechanism where breakdown to product of a zwitterionic tetrahedral intermediate is the rate-determining step. On the other hand, the β value for the reactions of BNPC is at the upper limit of those found for concerted mechanisms. The kinetic results for the reactions of anilines with BNPC correlates well with those for the concerted reactions of the same amines with 4-methylphenyl and 4-chlorophenyl 2,4-dinitrophenyl carbonates: A plot of the calculated log k_N values (through a multiple parametric equation) vs the experimental log k_N values is linear with unity slope and zero intercept, which confirms the concerted mechanism for the latter three reactions.

Introduction

Despite the fact that the kinetics and mechanisms of the aminolysis of alkyl aryl carbonates[1] and diaryl carbonates[2,3] have received much attention, the influence of the amine and leaving and nonleaving groups of the substrate on the kinetics and mechanism is still unclear. The kinetic investigations on the aminolysis of diaryl carbonates reported in the literature include the reactions of quinuclidines with nitrophenyl and dinitrophenyl phenyl carbonates in water,[2] the reactions of secondary alicyclic (SA) amines with 4-methylphenyl 4-nitrophenyl and 4-methylphenyl 2,4-dinitrophenyl carbonates (MPNPC and MPDNPC, respectively) in aqueous ethanol,[3a] and the reactions of the latter amines with phenyl 2,4-dinitrophenyl carbonate (PDNPC) in water.[3b] Also reported are the kinetics of the reactions of quinuclidines with MPNPC and 4-chlorophenyl 4-nitrophenyl carbonate (ClPNPC),[3c] and those of anilines with MPDNPC and 4-chlorophenyl 2,4-dinitrophenyl carbonate (ClPDNPC), all in aqueous ethanol.[3d]

The aminolysis (SA amines) of MPNPC in aqueous ethanol shows a nonlinear Brønsted-type plot with slopes $\beta_1 = 0.2$ (at high pK_a) and $\beta_2 = 0.9$ (at low pK_a), which was explained by a stepwise mechanism, through a zwitterionic tetrahedral intermediate ($T^{\pm}$), and a change in the rate-determining step with amine basicity.[3a] Similar results were obtained for the same aminolysis of ClPNPC in the same solvent.[3c] Nevertheless, the reactions of these amines with MPDNPC and ClPDNPC in aqueous ethanol were found to be concerted (a single step, without $T^{\pm}$).[3a,d] This was concluded on the basis of

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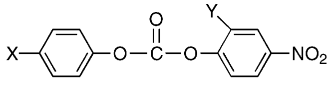
the slightly curved Brønsted plot found in the reactions of the former carbonate,[3a] and the linear Brønsted plot of slope 0.44 obtained in the SA aminolysis of ClPDNPC.[3d]

On the other hand, the quinuclidinolysis of MPNPC and ClPNPC show linear Brønsted plots of slopes ca. 0.9, consistent with a stepwise mechanism where $T^{\pm}$ decomposition is the rate-determining step.[3c]

Recently, we have investigated the reactions of anilines with MPDNPC and ClPDNPC in aqueous ethanol, where linear Brønsted plots of slopes 0.68 and 0.66 were obtained. These, together with other results, were explained by a concerted mechanism.[3d]

To clarify the mechanisms of the aminolysis of diaryl carbonates, in this work we study kinetically the reactions of anilines with bis(4-nitrophenyl) carbonate (BNPC), MPNPC and ClPNPC in aqueous ethanol. The main goal is to evaluate the influence of the amine nature and that of the leaving and nonleaving groups of the carbonate on the kinetics and mechanisms. This will be possible through a comparison of the kinetic results obtained in the title reactions in aqueous ethanol with those found in similar aminolyses in the same solvent.[3]



MPNPC (X = Me, Y = H)
ClPNPC (X = Cl, Y = H)
BNPC (X = NO_2, Y = H)
PDNPC (X = H, Y = NO_2)
MPDNPC (X = Me, Y = NO_2)
ClPDNPC (X = Cl, Y = NO_2)

Experimental Section

Materials. The anilines were purified either by distillation or recrystallization.[4] BNPC was a commercial product. MPNPC and ClPNPC were synthesized as reported.[3a,5] 4-Methylphenyl and 4-chlorophenyl *N*-phenyl carbamates, which are the products of the reactions of MPNPC and ClPNPC with unsubstituted aniline, were synthesized by the reactions of the corresponding chloroformate with aniline in acetonitrile.[3d]

Determination of p*K*a. The pK_a value of the conjugate acid of phenylenediamine was determined spectrophotometrically in 44 wt % ethanol−water, at 25.0 °C and an ionic strength of 0.2 (KCl).

Kinetic Measurements. The kinetics of the reactions were measured by a diode array spectrophotometer in 44 wt % ethanol−water solution, at 25.0 ± 0.1 °C and an ionic strength of 0.2 M (maintained with KCl), by monitoring (400 nm) the formation of 4-nitrophenoxide anion. The initial substrate concentration was 5×10^{-5} M. To maintain constant pH, phosphate buffer 0.01 M was employed in all reactions.

Under excess amine, pseudo-first-order rate coefficients (k_{obsd}) were found throughout. For the reactions of BNPC with the series of anilines the k_{obsd} values were obtained through the kinetic software (for first-order reactions) of the spectrophotometer. On the other hand, for the reactions of ClPNPC and MPNPC with the series of anilines, the k_{obsd} values were determined by the initial rate method,[6] due to the fact that these reactions are slow. Tables 1−3 show the experimental conditions of the reactions and the k_{obsd} values.

TABLE 1. Experimental Conditions and k_{obsd} Values for the Reactions of Anilines with Bis(4-nitrophenyl) Carbonate (BNPC)[a]

amine	pH	$10^3[N]_{tot}{}^b$/M	10^3k_{obsd}/s^{-1}	no. of runs
4-phenylenediamine	7.0	5.00−42.5	2.11−13.5	6
	7.2	5.00−42.5	2.50−15.2	6
	7.5	5.00−50.0	3.11−19.3	7
4-methoxyaniline	7.0	10.0−100	0.899−5.83	7
	7.2	10.0−100	0.920−6.35	7
	7.5	10.0−100	1.05−6.56	7
4-methylaniline	7.0	10.0−100	0.632−3.28	7
	7.2	10.0−100	0.683−3.39	7
	7.5	10.0−100	0.729−3.62	7
aniline	7.0	5.00−85.0	0.396−1.44	6
	7.2	5.00−100	0.431−1.45	7
	7.5	5.00−100	0.435−1.45	7
3-aminoacetophenone	7.0	2.50−25.0	0.411−0.455	6
	7.2	2.50−25.0	0.450−0.520	7
	7.5	2.50−25.0	0.484−0.540	7
3-aminobenzonitrile	6.8	12.5−85.0	0.446−0.472	5
	7.0	50.0−170	0.394−0.449	5

[a] In 44 wt % ethanol−water, at 25.0 °C, ionic strength 0.2 (KCl), in the presence of phosphate buffer 0.01M. [b] Concentration of total amine (free base plus protonated forms).

Product Studies. 4-Nitrophenoxide anion was identified as one of the products of the reactions, by comparison of the UV−vis spectra at the end of the reactions with an authentic sample of 4-nitrophenol, at the kinetic conditions. 4-Methylphenyl and 4-chlorophenyl *N*-phenylcarbamates were found as the other product of the reactions of MPNPC and ClPNPC with unsubstituted aniline, respectively, as shown by HPLC, using as reference the corresponding carbamate. HPLC conditions: column Eurospher C-18 (10 cm, 7 μm), eluant acetonitrile/water = 70/30, isocratic mode 0.5 mL/min.

Results and Discussion

The title reactions were found to be ruled by the rate equations depicted in eqs 1 and 2, where NPO- and S represent 4-nitrophenoxide and the substrate, respectively, and k_{obsd}, k_0, and k_N are the pseudo-first-order, the solvolysis, and the anilinolysis rate coefficients, respectively.

$$\frac{d[NPO^-]}{dt} = k_{obsd}[S] \qquad (1)$$

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

The values of k_0 and k_N were obtained as intercept and slope, respectively, of the linear plots of k_{obsd} vs [amine], at constant pH. The k_N values show independence of pH. For the slowest reactions, where the k_0 term was important compared with k_N [amine] in eq 2, the k_0 values are dependent on pH.

Table 4 shows the values of k_N for the reactions of anilines with BNPC, MPNPC, and ClPNPC, along with the pK_a values of the conjugate acids of these amines. The k_N and pK_a values were statistically corrected with $q = 1$ for all the anilines, except phenylenediamine with $q = 2$, and $p = 3$ for the conjugate acids of all anilines.[3d,7] The statistical parameter q is the number of equivalent basic sites of the amine and p is the number of equivalent

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TABLE 2. Experimental Conditions and k_{obsd} Values for the Reactions of Anilines with 4-Chlorophenyl 4-Nitrophenyl Carbonate (ClPNPC)[a]

amine	pH	10^3 [N]$_{tot}$[b]/M	10^5 k_{obsd}/s^{-1}	no. of runs
4-phenylenediamine	7.2	1.25−5.88	9.61−32.9	4
	7.5	1.25−9.73	10.6−43.4	6
4-methoxyaniline	7.0	8.70−87.0	5.21−68.5	7
	7.2	8.70−73.8	4.82−71.3	6
	7.5	8.70−73.8	10.8−67.3	6
4-methylaniline	7.0	5.00−42.5	1.87−5.90	6
	7.2	5.00−42.5	3.21−8.62	6
	7.5	5.00−42.5	4.20−11.3	6
aniline	7.0	54.0−460	10.6−49.7	6
	7.2	54.0−460	9.21−56.3	6
	7.5	54.0−460	9.95−60.2	6
3-aminoacetophenone	7.0	50.0−200	0.99−2.25	6
	7.2	70.0−200	2.05−3.15	8
	7.5	10.0−200	3.29−5.00	8

[a] In 44 wt % ethanol−water, at 25.0 °C, ionic strength 0.2 (KCl), in the presence of phosphate buffer 0.01 M. [b] Concentration of total amine (free base plus protonated forms).

TABLE 3. Experimental Conditions and k_{obsd} Values for the Reactions of Anilines with 4-Methylphenyl 4-Nitrophenyl Carbonate (MPNPC)[a]

amine	pH	10^3 [N]$_{tot}$[b]/M	10^5 k_{obsd}/s^{-1}	no. of runs
4-phenylenediamine	7.2	1.25−6.88	3.04−16.4	4
	7.5	1.25−8.75	3.85−18.6	5
4-methoxyaniline	7.0	8.7−87	1.98−12.7	7
	7.2	8.7−73.8	1.85−13.9	6
	7.5	8.7−87	2.49−15.4	6
4-methylaniline	7.2	5−42.5	0.64−3.30	6
	7.5	5−42.5	1.46−4.89	6
aniline	7.0	54−460	6.00−16.3	6
	7.2	54−460	4.50−20.2	6
	7.5	54−460	4.40−12.2	4

[a] In 44 wt % ethanol−water, at 25.0 °C, ionic strength 0.2 (KCl), in the presence of phosphate buffer 0.01 M. [b] Concentration of total amine (free base plus protonated forms).

TABLE 4. Values of pK_a for the Conjugate Acids of Anilines and k_N Values for the Reactions of These Amines with Bis(4-nitrophenyl) Carbonate (BNPC), 4-Methylphenyl 4-Nitrophenyl Carbonate (MPNPC), and 4-Chlorophenyl 4-Nitrophenyl Carbonate (ClPNPC)[a]

		10^3k_N/s^{-1} M^{-1}		
amine	pK_a	BNPC	MPNPC	ClPNPC
4-phenylene-diamine	6.45	410 ± 14	22 ±1	39 ± 2
4-methoxyaniline	5.29	59 ± 2	1.7 ± 0.2	9.0 ± 0.5
4-methylaniline	4.90	31 ± 1	0.8 ± 0.1	1.7 ± 0.2
aniline	4.46	11.5 ± 0.4	0.30± 0.02	1.14 ± 0.04
3-amino-acetophenone	3.10	2.6 ± 0.5		0.087 ± 0.005
3-amino-benzonitrile	2.12	0.43 ± 0.05		

[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).

protons of the conjugate acid of the amine.[7] The statistically corrected Brønsted-type plots are shown in Figure 1. The plots are linear, with slopes $\beta = 0.65$, 0.85, and 0.78 for the anilinolysis of BNPC, MPNPC, and ClPNPC, respectively.

The k_N values obtained for the reactions of anilines are in the sequence BNPC > ClPNPC > MPNPC. This can be attributed to the order of electron-withdrawing abilities of the substituents in the nonleaving group: 4-NO_2 (in BNPC) > 4-Cl (in ClPNPC) > 4-Me (in MPNPC). This makes BNPC more susceptible toward amine attack than ClPNPC and MPNPC.[8]

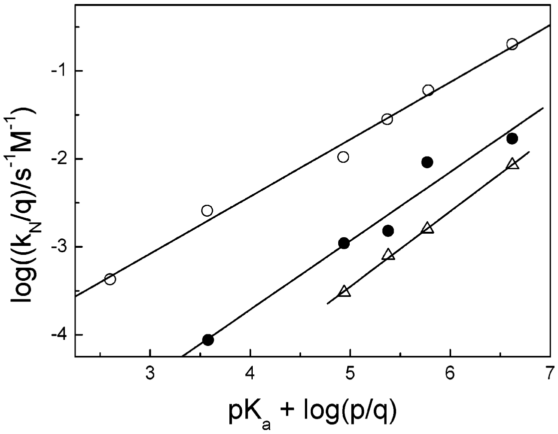

FIGURE 1. Brønsted-type plots (statistically corrected) obtained in the reactions of anilines with BNPC (○), MPNPC (△), and ClPNPC (●) in 44 wt % ethanol−water, at 25.0 °C and an ionic strength of 0.2 M. The slopes (β) are 0.65, 0.85, and 0.78, respectively.

The value of $\beta = 0.65$ found for the reactions of BNPC is just below the lower limit of the Brønsted slopes obtained in stepwise aminolysis (β_2) of similar carbonates and esters and their thio analogues when decomposition to products of the zwitterionic tetrahedral intermediate ($T^{\pm}$) is rate-limiting. The usual slope range in these cases is $\beta_2 = 0.8-1$,[1a−d,2,6a,9] but only in some few cases the lower limit of β_2 has been 0.7.[10]

On the other hand, for concerted mechanisms, usually linear Brønsted plots with slopes 0.4−0.7 have been found.[9] Among the concerted aminolysis exhibiting slope values near that found in the anilinolysis of BNPC ($\beta =$ 0.65, this work) are the following: the pyridinolysis of *N*-methoxycarbonylisoquinolinium ion ($\beta = 0.58$),[11] the reactions of SA amines with ethyl 2,4-dinitrophenyl thiolcarbonate($\beta = 0.56$),[12] and the reactions of anilines with MPDNPC ($\beta = 0.68$)[3d] and ClPDNPC ($\beta = 0.66$).[3d]

Nevertheless, the value of the Brønsted slope is not of itself sufficient to prove that a reaction is concerted.[13] Although the anilinolysis of BNPC seems to be in the borderline between stepwise and concerted mechanisms, we think that this reaction is more likely to be concerted on the basis of the argument below.

A multiparametric equation can be derived using the k_N values obtained in the anilinolyses of BNPC (this work), MPDNPC, and ClPDNPC,[3d] together with the pK_a values of the conjugate acids of the nucleophiles, nucleofuges and nonleaving groups. The pK_a values employed are those in water and 25 °C: pK_a = 10.3, 9.4, 7.1, and 4.1 for 4-methylphenol, 4-chlorophenol, 4-nitrophenol, and 2,4-dinitrophenol, respectively.[14] This equation (sta-

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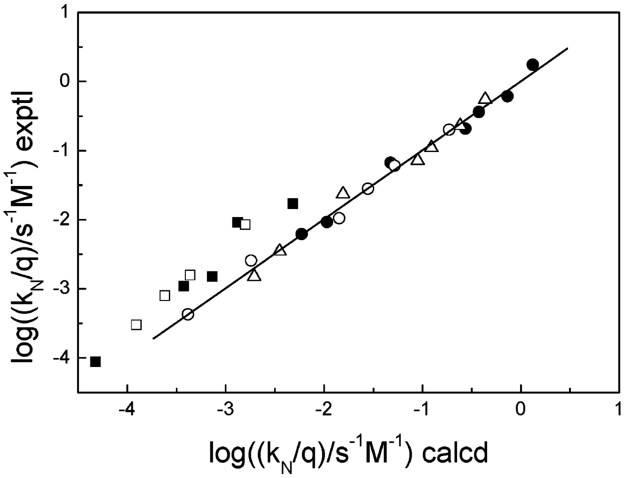


FIGURE 2. Plot of experimental log k_N/q vs calculated (through eq 3) log k_N/q for the concerted reactions of anilines with BNPC (○), ClPDNPC (●), and MPDNPC (△) and the stepwise reactions of anilines with ClPNPC (■) and MPNPC (□) in 44 wt % ethanol−water, at 25.0 °C and an ionic strength of 0.2 (KCl).

tistically corrected for k_N and pK_a of anilines) is shown in eq 3 ($n = 20$, $R^2 = 0.991$). In this equation N, nlg, and lg correspond to the nucleophile, nonleaving group, and leaving group, respectively, and pK_a(N)$_{corr}$ is pK_a(N) + log p/q; the pK_a coefficients (β) are subjected to an error of ± 0.1.

$$\log k_N/q = 6.9 + 0.66\mathrm{p}K_a(\mathrm{N})_{corr} - 0.69\mathrm{p}K_a(\mathrm{nlg}) - 1.0\mathrm{p}K_a(\mathrm{lg}) \quad (3)$$

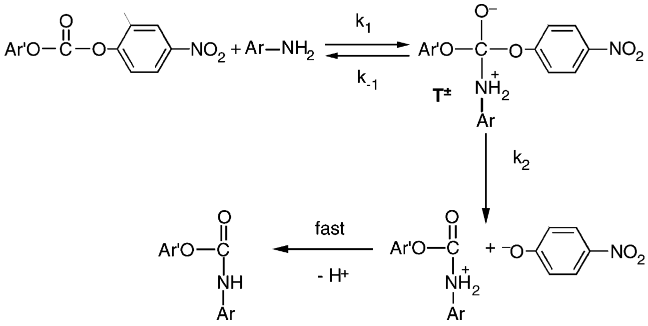
Figure 2 shows a plot of experimental log k_N against calculated (through eq 3) log k_N; the plot is linear with unity slope and zero intercept. This figure also shows the corresponding plot for the anilinolysis of MPNPC and ClPNPC (see below).

It has been shown that the reactions of anilines with MPDNPC and ClPDNPC in aqueous ethanol are concerted.[3d] Therefore, the good correlation exhibited by the anilinolysis of BNPC with the other concerted reactions (Figure 2) suggests that the anilinolysis of BNPC is also concerted. Furthermore, the sensitivity of log k_N to the basicity of the nucleophile and nonleaving group (β_N = 0.66 and $\beta_{nlg} = -0.69$ in eq 3) are the same as those obtained in a similar plot considering only the anilinolysis of MPDNPC and ClPDNPC.[3d] This further suggests that the reactions of anilines with BNPC in aqueous ethanol are driven by a concerted mechanism.

The reactions of anilines with ClPNPC and MPNPC show linear Brönsted-type plots (Figure 1) with slopes β 0.78 and 0.85, respectively. These slope values are consistent with a pathway through a zwitterionic tetrahedral intermediate (T$^\pm$) whose breakdown to products is rate determining.[1a−d,2,6a,9,10] A dual parametric equation obtained with the k_N values for these reactions and the pK_a values of the conjugate acids of the anilines and nonleaving groups is shown in eq 4 ($n = 9$, $R^2 = 0.969$). A plot of experimental log k_N against calculated (through eq 4) log k_N is linear with unity slope and zero intercept (plot not shown).

$$\log(k_N/q) = -0.5 + 0.8\mathrm{p}K_a(\mathrm{N})_{corr} - 0.68\mathrm{p}K_a(\mathrm{nlg}) \quad (4)$$

SCHEME 1



An additional proof that the anilinolyses of ClPNPC and MPNPC are stepwise is the following: A plot of the experimental log(k_N/q) values vs those calculated through eq 3 is shown in Figure 2, together with the same plot for the concerted anilinolysis of BNPC, ClPDNPC and MPDNPC. As seen in this figure, the experimental log(k_N/q) values for the reactions of ClPNPC and MPNPC are greater than those predicted for the hypothetical concerted mechanism (those on the line for the concerted reactions of the other carbonates). This means that the stepwise path is preferred over the concerted one for the anilinolysis of ClPNPC and MPNPC.

Therefore, according to the above arguments, it is likely that the anilinolysis of ClPNPC and MPNPC behave according to Scheme 1, where the formation of T$^\pm$ is an equilibrium step and the k_2 step is rate limiting ($k_{-1} \gg k_2$ in Scheme 1) for the whole pK_a range of anilines.

If the reactions of anilines with MPNPC and ClPNPC in aqueous ethanol are stepwise (this work) and those of MPDNPC and ClPDNPC in the same solvent are concerted,[3d] it means that addition of a second nitro group to the nucleofuge destabilizes the zwitterionic tetrahedral intermediate (T$^\pm$) to such an extent as to produce a change in the mechanism from stepwise to concerted. This destabilization of T$^\pm$ should be due to the greater nucleofugality of 2,4-dinitrophenoxide from T$^\pm$ compared to that of 4-nitrophenoxide. On the other hand, according to the results in this work, substitution of Me or Cl by NO$_2$ as the para substituent in the nonleaving group also brings a great destabilization of the T$^\pm$ intermediate and causes a change in mechanism, from stepwise to concerted. This could be due to the fact that BNPC possesses two good leaving groups that can destabilize T$^\pm$ kinetically. These results are in accordance with the prediction derived from the global electrophilicity of substrates, determined by Parr's method.[15] According to this method, the global electrophilicity of BNPC is greater than those of the other nitrophenyl carbonates.[15] The values (in ev) for the above carbonates are: ClPDNPC (1.30), MPDNPC (1.16), BNPC (1.09), ClPNPC (0.84), and MPNPC (0.84). Since the value for BNPC is closer to that for MPDNPC than that for ClPNPC and MPNPC, it is likely that the reactions of anilines with BNPC be ruled by the same

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mechanism operating for the anilinolysis of MPDNPC (concerted) rather than the mechanism for the anilinolysis of the mononitro carbonates, ClPNPC and MPNPC.

On the other hand, the reactions of SA amines and quinuclidines (tertiary alicyclic amines) with MPNPC and ClPNPC in aqueous ethanol are all governed by stepwise mechanisms.[3a,c] It is known that these amines are better nucleofuges from the T$^{\pm}$ intermediate than isobasic anilines.[16] Therefore, anilines should stabilize this intermediate relative to isobasic SA amines and quinuclidines. Since the reactions of these latter amines with MPNPC and ClPNPC are stepwise, it is even more likely that the reactions of anilines be stepwise, as found in this work.

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