

Kinetics and Mechanism of the Aminolysis of 4-Methylphenyl and 4-Chlorophenyl 4-Nitrophenyl Carbonates in Aqueous Ethanol

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Reactions of 4-methylphenyl 4-nitrophenyl carbonate (MPNPC) and 4-chlorophenyl 4-nitrophenyl carbonate (CIPNPC) with a series of quinuclidines (QUIN) and the latter carbonate with a series of secondary alicyclic amines (SAA) are subjected to a kinetic investigation in 44 wt % ethanolwater, at 25.0 °C and an ionic strength of 0.2 M. The reactions were followed spectrophotometrically at 330 or 400 nm (4-nitrophenol or 4-nitrophenoxide anion appearance, respectively). Under excess amine, pseudo-first-order rate coefficients (k_{obsd}) are found. For all these reactions, plots of k_{obsd} vs free amine concentration at constant pH are linear, the slope (k_N) being independent of pH. The Brönsted-type plots (log k_N vs p K_a of the conjugate acids of the amines) for the reactions of the series of QUIN with MPNPC and ClPNPC are linear with slopes (β_N) 0.88 and 0.87, respectively, which are explained by a stepwise process where breakdown of a zwitterionic tetrahedral intermediate (T^{\pm}) to products is rate limiting. The Brönsted-type plot for the reactions of the series of SAA with ClPNPC is biphasic with slopes $\beta_1 = 0.2$ (high pK_a region) and $\beta_2 = 0.9$ (low pK_a region) and a curvature center at $pK_a^0 = 10.6$. This plot is in accordance with a stepwise mechanism through T^{\pm} and a change in the rate-determining step, from T^{\pm} breakdown to T^{\pm} formation as the basicity of the SAA increases. Two conclusions arise from these results: (i) QUIN are better leaving groups from T[±] than isobasic SAA, and (ii) the nonleaving group effect on k_N for these reactions is small, since β_{nlg} ranges from -0.2 to -0.3. From these values, it is deduced that ClPNPC is ca. 70% more reactive than MPNPC toward SAA and QUIN, when expulsion of the leaving group from T[±] is the rate determining step.

Introduction

The kinetics and mechanism of the aminolysis of aryl esters is well documented;¹ nevertheless, the mechanism of the aminolyses of alkyl aryl carbonates²⁻⁴ and diaryl carbonates^{3c,5,6} have received little attention. The latter reports concern the reactions of secondary alicyclic amines (SAA) with phenyl 2,4-dinitrophenyl carbonate,^{3c} quinuclidines (QUIN) with 3-nitrophenyl, 4-nitrophenyl, 3.4-dinitrophenyl, and 2.4-dinitrophenyl phenyl carbonates,⁵ and the reactions of SAA with 4-nitrophenyl and 2,4-dinitrophenyl 4-methylphenyl carbonates.⁶ Some of these reactions have been described as stepwise, through a zwitterionic tetrahedral intermediate (T^{\pm}), due to the biphasic Brönsted-type plots obtained.⁵ These biphasic plots show two linear portions, at low (with slope $\beta = 1$) and high ($\beta = 0.3$) amine p K_a values, which have been assigned to rate-determining breakdown and formation of T[±], respectively.⁵

Other aminolysis reactions of diaryl carbonates have been found to be concerted, i.e., with no intermediate, in a single step. This is the case of the reactions of SAA with phenyl 2,4-dinitrophenyl carbonate^{3c} and with 4-methylphenyl 2,4-dinitrophenyl carbonate.⁶ The former reaction exhibits a linear Brönsted-type plot with slope $\beta = 0.4$,^{3c} and the latter shows a slightly curved plot, with $\beta = 0.1$ and $\beta = 0.5$ at high and low amine pK_a, respectively.6

With the aim to clarify the mechanism of the aminolysis of diaryl carbonates, in this work we report a kinetic investigation of the reactions of 4-methylphenyl 4-nitrophenyl carbonate (MPNPC) and 4-chlorophenyl 4-nitrophenyl carbonate (ClPNPC) with a series of QUIN and

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TABLE 1.	Experimental	Conditions and	kobsd Value	s for Reaction	ns of a Series o	f QUIN with 4-M	ethylphenyl
4-Nitrophe	nyl Carbonate	(MPNPC) ^a					

amine	pH	$F_{ m N}{}^b$	10 ³ [N] _{tot} (M) ^c	$10^3 k_{\rm obsd} \ ({\rm s}^{-1})$	number of runs
quinuclidine	10.36	0.33	1.24-15.0	2.80 - 44.9	6
	10.66	0.50	1.25 - 15.0	4.88 - 72.8	7
	10.96	0.67	1.26 - 12.0	6.71-89.0	7
3-hydroxyquinuclidine	9.0	0.169	0.667 - 8.00	0.512 - 5.70	7
	9.3	0.289	1.00 - 12.0	0.900 - 10.7	6
	9.6	0.448	1.33 - 16.5	2.10 - 15.0	7
3-chloroquinuclidine	7.5	0.33	4.20 - 50.0	0.0867 - 0.812	7
	7.8	0.50	14.1 - 85.6	0.375 - 1.96	6
	8.1	0.67	16.6 - 56.8	0.475 - 1.52	6
3-quinuclidinone	6.8	0.33	87.6-150	0.182 - 0.311	7
	7.1	0.50	50.0 - 175	0.218 - 0.559	6
	7.4	0.67	50.0-170	0.270 - 0.745	6

^{*a*} In 44 wt % ethanol–water, at 25.0 °C, ionic strength = 0.2 M (KCl). ^{*b*} Free amine fraction. ^{*c*} Concentration of total amine (free base plus protonated forms).

the latter carbonate with a series of SAA. By comparison of the kinetic results obtained in this work with those for the aminolysis of other carbonates, we evaluate the effect of the nonleaving group of the substrate and the amine nature on the kinetics and mechanism of these reactions.



Experimental Section

Materials. The SAA and QUIN series of amines were purified as reported.^{5,7} The substrates, MPNPC⁶ and ClPNPC,⁸ were synthesized as described in the literature.^{6,8} One of the products of the reaction of ClPNPC with morpholine, 1-(4-chlorophenoxycarbonyl)morpholine, was synthesized by the reaction of 4-chlorophenyl chloroformate with morpholine, in acetonitrile, according to a general method.⁹ This product melted at 76.8–77.3 °C (lit.¹⁰ mp 80.0 °C) and was identified by ¹H NMR, ¹³C NMR, and IR analyses.

Determination of pK_a. The p K_a values of the conjugate acids of quinuclidine and 3-hydroxyquinuclidine were determined spectrophotometrically, and those of 3-chloroquinuclidine and 3-quinuclidinone were measured potentiometrically, all of them in 44 wt % ethanol-water solution, at 25.0 \pm 0.1 °C and an ionic strength 0.2 (KCl).

Kinetic Measurements. The kinetics of the reactions were analyzed through a diode array spectrophotometer in 44 wt % ethanol-water, at 25.0 ± 0.1 °C and an ionic strength of 0.2 M (maintained with KCl). The reactions were followed at 400 nm (appearance of 4-nitrophenoxide anion), except the reaction of ClPNPC with piperazinium ion, which was carried out at a low pH, following at 330 nm the appearance of 4-nitrophenol.

All reactions were studied under at least a 12-fold amine excess over the substrate, the initial concentration being 2.5 $\times~10^{-5}$ M. Under these conditions, pseudo-first-order rate

coefficients (k_{obsd}) were found throughout, the reactions being followed for at least 5 half-lives.

For all of the reactions, the pH was maintained constant (three pH values for each amine) by the buffer formed by partial protonation of the amine.

The k_{obsd} values and the experimental conditions for the reactions of MPNPC with the series of QUIN are exhibited in Table 1. Those for the reactions of ClPNPC with the series of SAA and QUIN are shown in Table 2.

Product Studies. 4-Nitrophenoxide anion (and/or its conjugate acid in the reactions at pH lower than ca. 7) was identified as one of the products of the aminolyses of MPNPC and CIPNPC. This was carried out by comparison of the UVvis spectra after completion of these reactions with that of an authentic sample of sodium 4-nitrophenoxide, under the kinetic conditions. The other product of the reactions of MPNPC and ClPNPC with 3-hydroxyquinuclidine was identified as the corresponding carbamate. This was achieved by comparison of the UV-vis spectra after completion of these reactions with those at the end of the reactions of 3-hydroxyquinuclidine with 4-methylphenyl and 4-chlorophenyl chloroformates, respectively. The other product of the reaction of ClPNPC with morpholine was identified as 1-(4-chlorophenoxycarbonyl)morpholine, by comparison of the HPLC retention time of the product after completion of the reaction with that of an authentic sample. HPLC conditions: column, Supelcosil LC-18-DB (25 cm, 5 μ m); eluant, acetonitrile/water= 50/50; isocratic mode, 0.4 mL/min.

Results and Discussion

The pseudo-first-order rate constants (k_{obsd}) obtained, under excess amine, for all of the reactions obey eq 1, where k_0 and k_N are the rate coefficients for solvolysis and aminolysis of the substrates, respectively. The values of k_0 and k_N show no dependence on pH within the pH range employed. These values were obtained as the intercept and slope, respectively, of linear plots of k_{obsd} against free amine concentration ([free amine]) at constant pH.

$$k_{\text{obsd}} = k_0 + k_{\text{N}} [\text{free amine}] \tag{1}$$

For the reactions of MPNPC, the k_0 values were negligible, except in the reactions with quinuclidine and 3-hydroxyquinuclidine (ca. 0.0001 s⁻¹), although they were subjected to large errors. For the reactions of ClPNPC, the k_0 values were significant in the reactions with piperidine, piperazine, quinuclidine and 3-hydroxyquinuclidine (ca. 0.001 s⁻¹) and in the reaction with

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TABLE 2.	Experimental	Conditions	and <i>k</i> obsd	Values for	Reactions	of a Series	of SAA and	QUIN with	4-Chlorophenyl
4-Nitropher	nyl Carbonate	(ClPNPC) ^a							

t		E h	103 [N] (M)(103 h (c ⁻¹)	number
amme	рн	$P_{\rm N}^{\rm S}$	10° [IN] _{tot} (IVI)°	$10^{\circ} K_{\text{obsd}} (\text{S}^{-1})$	of runs
piperidine	10.52	0.33	0.30 - 3.0	18.0-100	9
	10.82	0.50	0.30 - 3.0	23.0 - 140	10
	11.12	0.67	0.30 - 3.0	28.0 - 200	10
piperazine	9.41	0.33	1.0 - 10.0	7.10-83.0	10
	9.71	0.50	1.0 - 10.0	13.0-130	10
	10.01	0.67	1.0 - 10.0	19.0-170	10
1-(2-hydroxyethyl)piperazine	8.79	0.33	6.0 - 60.0	12.0-110	10
	9.09	0.50	6.0 - 60.0	19.0-190	9
	9.39	0.67	6.0 - 60.0	28.0 - 250	14
morpholine	8.18	0.33	10.0-100	13.0 - 97.0	10
-	8.48	0.50	10.0-100	18.0-170	10
	8.78	0.67	10.0-100	23.0 - 220	10
1-formylpiperazine	7.33	0.33	10.0-100	1.20 - 9.20	10
	7.63	0.50	10.0-100	1.70 - 15.0	10
	7.93	0.67	10.0-100	2.70 - 19.0	10
piperazinium ion	5.07	0.33	10.0 - 90.0	0.053 - 0.240	9
	5.37	0.50	10.0-100	0.062 - 0.340	10
	5.67	0.67	10.0 - 100	0.094 - 0.510	10
quinuclidine	10.36	0.33	1.24 - 15.0	7.58 - 71.5	6
	10.66	0.50	1.25 - 15.0	10.5 - 110	7
	10.96	0.67	1.26 - 12.0	7.72-101	6
3-hydroxyquinuclidine	9.0	0.169	0.667 - 8.00	0.766 - 9.49	7
	9.3	0.289	1.00 - 10.0	1.09 - 11.0	6
	9.6	0.448	1.33 - 15.9	2.21-19.3	6
3-chloroquinuclidine	7.5	0.33	8.40 - 50.0	0.231 - 1.17	7
	7.8	0.50	14.1 - 100	0.671 - 3.58	7
	8.1	0.67	16.6 - 71.2	0.824 - 3.13	7
3-quinuclidinone	6.8	0.33	87.6-150	0.329 - 0.571	7
-	7.1	0.50	25.0 - 175	0.144 - 0.788	7
	7.4	0.67	25.0 - 170	0.174 - 0.997	7

^{*a*} In 44 wt % ethanol–water, at 25.0 °C, ionic strength = 0.2 M (KCl). ^{*b*} Free amine fraction. ^{*c*} Concentration of total amine (free base plus protonated forms).

TABLE 3. Values of pKa for Conjugate Acids of	
Quinuclidines (QUIN) and <i>k</i> _N Values for Reactions of	
QUIN with 4-Methylphenyl 4-Nitrophenyl Carbonate	
(MPNPC) and 4-Chlorophenyl 4-Nitrophenyl Carbonate	ļ
(CIPNPC) ^a	

		$10^2 k_{\rm N} \ ({ m s}^{-1} \ { m M}^{-1})$				
amine	pKa	MPNPC	ClPNPC			
quinuclidine 3-hydroxyquinuclidine 3-chloroquinuclidine 3-quinuclidinone	10.66 9.7 7.8 7.1	$\begin{array}{c} 930\pm 30\\ 136\pm 3\\ 4.4\pm 0.2\\ 0.62\pm 0.002 \end{array}$	$\begin{array}{c} 1360\pm 60\\ 170\pm 5\\ 7.0\pm 0.2\\ 0.80\pm 0.03\end{array}$			

 a Both the pK_a and $k_{\rm N}$ values were determined in 44 wt % ethanol–water, at 25.0 °C, ionic strength = 0.2 M (KCl).

piperazinium ion (ca. 0.00002 s⁻¹). These k_0 values were much smaller than the aminolysis term (k_N [free amine] in eq 1) and also subjected to large errors.

The k_N values obtained for the quinuclidinolysis of MPNPC and CIPNPC are shown in Table 3; the corresponding Brönsted plots can be seen in Figure 1.

The values of $k_{\rm N}$ for the reactions of SAA with ClPNPC are shown in Table 4. These values, as well as those of the $pK_{\rm a}$ of the conjugate acids of the amines, were statistically corrected with q = 2 for piperazine (q = 1for all other SAA) and p = 2 for all the conjugate acids of the amines, except that for piperazinium ion with p =4.^{11,12} The parameter q is the number of equivalent basic



FIGURE 1. Brönsted-type plots for the quinuclidinolysis of MPNPC (\bigcirc) and ClPNPC (\bigcirc) in 44 wt % ethanol-water, at 25.0 °C, ionic strength = 0.2 M (KCl). The slopes (β) are 0.88 and 0.87, respectively.

sites on the free amine, and p is the number of equivalent dissociable protons on the conjugate acid of the amine.¹² With these corrected values, the Brönsted-type plot was drawn (see Figure 2). For comparison, Figure 2 also shows the Brönsted-type plot obtained for the reactions of the same amines with MPNPC in the same solvent.⁶

The reactions of MPNPC and ClPNPC with the series of QUIN show linear Brönsted-type plots (Figure 1) of slopes $\beta = 0.88 \pm 0.08$ and 0.87 ± 0.06 , respectively. From the magnitude of these slopes, it can be deduced that

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SCHEME 1

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TABLE 4. Values of pK_a for Conjugate Acids of Secondary Alicyclic Amines (SAA) and k_N Values for Reactions of SAA with 4-Chlorophenyl 4-Nitrophenyl Carbonate (CIPNPC)^a

amine	pK _a	$k_{\rm N}~({ m s}^{-1}~{ m M}^{-1})$
piperidine	10.82	89 ± 3
piperazine	9.71	26 ± 0.3
1-(2-hydroxyethyl)piperazine	9.09	6.1 ± 0.1
morpholine	8.48	3.1 ± 0.1
1-formylpiperazine	7.63	0.28 ± 0.01
piperazinium ion	5.37	0.0072 ± 0.0003

^a Both the	pKa	and	$k_{\rm N}$	values	were	deter	rmined	in 4	4	wt	%
ethanol-wat	er, at	25.0	°C,	, ionic s	trengt	th = 0	0.2 M (I	KCl)			



FIGURE 2. Brönsted-type plots (statistically corrected, see text) for the reactions of SAA with MPNPC (O, ref 6) and ClPNPC (●, this work) in 44 wt % ethanol-water, at 25.0 °C, ionic strength = 0.2 M (KCl).

these reactions proceed by a stepwise mechanism, i.e., through the formation of a zwitterionic tetrahedral intermediate (T^{\pm}) whose breakdown to products is the rate-limiting step (see Scheme 1).^{2,5-7,11}

A plot (not shown) of log $k_{\rm N}$ for the quinuclidinolysis of CIPNPC vs log $k_{\rm N}$ for the same aminolysis of MPNPC is linear, according to eq 2 (n = 4; $R^2 = 0.995$). The magnitude of this intercept indicates that CIPNPC is ca. 70% more reactive toward a given QUIN than its 4-methyl derivative. Since for these reactions the k_2 step of Scheme 1 is rate determining, it follows that $k_N = k_1 k_2/k_2$ k_{-1} , where k_1/k_{-1} is the equilibrium constant for the first step of this scheme. The larger $k_{\rm N}$ for the reaction of a given QUIN with CIPNPC than that with MPNPC can be attributed to a larger k_1 value for the former reaction since there seems to be little influence of the substituents 4-Cl and 4-Me on the k_2/k_{-1} ratio (see below).

$\log k_{\rm N} \text{ (ClPNPC)} = \log k_{\rm N} \text{ (MPNPC)} + 0.24 \quad (2)$

With the $k_{\rm N}$ values found in the present reactions of QUIN together with the pK_a values of the conjugate acids of the nucleophiles, and the nonleaving groups (10.1 and 9.4 for 4-methylphenol and 4-chlorophenol in water, respectively), eq 3 can be deduced by dual regression analysis (n = 8, $R^2 = 0.992$). In this expression, N and nlg refer to the nucleophile and the nonleaving group, respectively; the $pK_a(N)$ and $pK_a(nlg)$ coefficients (β_N and β_{nlg} , respectively) are both subjected to an error of \pm 0.1.

$$\log k_{\rm N} = -6.2 + 0.87 p K_{\rm a}({\rm N}) - 0.20 p K_{\rm a}({\rm nlg}) \quad (3)$$

The sensitivity of log $k_{\rm N}$ to the nonleaving group ($\beta_{\rm nlg}$ = -0.2) is similar to that obtained for log k_1 for the reactions of the series of SAA with aryl 4-nitrophenyl thionocarbonates ($\beta_{nlg} = -0.2 \pm 0.1$).¹³ Assuming that the latter value can be extended to carbonates, and since this value measures the sensitivity on $pK_a(nlg)$ of log k_1 and the former that of $\log k_N$ (where $k_N = k_1 k_2 / k_{-1}$), the value of β_{nlg} for k_2/k_{-1} must be 0 ± 0.2 . Namely, there seems to be little or no influence of the above nonleaving group substituents on the k_2/k_{-1} ratio. It is reasonable that all these values of β_{nlg} are small (for both rate-limiting steps) since there should be little charge development on the oxygen atom of the nonleaving group in going from the substrate to the corresponding transition state,⁵ since the bond between the oxygen (nlg) and the central carbon is not being broken.

The above result is in accordance with the finding of Gresser and Jencks for the quinuclidinolysis of diaryl carbonates in water.¹⁴ They found that there is little effect of the nonleaving group substituents on the k_2/k_{-1} ratio ($\beta_{nlg} = 0.2 \pm 0.04$).^{14,15} Since it is known that the inductive effect is the most important one for groups attached to the central carbon of a T^{\pm} intermediate, 16 this means that inductively electron-donating substituents attached to the nonleaving group of T^{\pm} slightly favor aryloxide leaving from T[±] relative to amine expulsion.¹⁴

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A logarithmic plot (not shown) of the experimental $k_{\rm N}$ vs calculated $k_{\rm N}$ (through eq 3) for the reactions of both substrates with QUIN is linear through the origin; the slope is 1.00 ± 0.04 (n = 8, $R^2 = 0.992$). The good fit and unity slope indicates that both reactions follow the same mechanism (stepwise) with the same rate-limiting step (k_2 step in Scheme 1).

The curved Brönsted plot obtained for the reactions of the series of SAA with CIPNPC (Figure 2), as well as that found for the same aminolysis of MPNPC,⁶ are in accordance with a stepwise mechanism (shown in Scheme 2, where NH represents a SAA) through a zwitterionic tetrahedral intermediate (T[±]). These curved plots can be explained assuming that for weakly basic nucleophiles, $k_{-1} > k_2$, and therefore step k_2 is rate limiting in these cases. For strongly basic nucleophiles, $k_{-1} < k_2$, and formation of T[±] (step k_1) is rate determining.^{2,3a,5-7,11}

The line in Figure 2 for the reactions of SAA with ClPNPC was calculated (as well as that for the reactions of the same amines with MPNPC)⁶ through a semiempirical equation (eq 4) based on the above change in the rate-determining step.^{2b,c,5-7}

$$\log(k_{\rm N}/k_{\rm N}^{\circ}) = \beta_2(pK_{\rm a} - pK_{\rm a}^{\circ}) - \log[(1 + {\rm a})/2]$$
$$\log {\rm a} = (\beta_2 - \beta_1)(pK_{\rm a} - pK_{\rm a}^{\circ})$$
(4)

As a result of the fitting, the following parameters were obtained for the reactions of CIPNPC: log $k_{\rm N}^0 = 1.71 \pm 0.1$, $pK_{\rm a}^0 = 10.6 \pm 0.2$, $\beta_1 = 0.2 \pm 0.1$, and $\beta_2 = 0.9 \pm 0.1$ (n = 6, $R^2 = 0.995$). The parameters $k_{\rm N}^0$ and $pK_{\rm a}^0$ correspond to an (hypothetical) amine that leaves T[±] as fast as the leaving group of the substrate ($k_{-1} = k_2$), and β_1 and β_2 are the slopes at high and low amine $pK_{\rm a}$ values, respectively. The latter values agree with those found for rate-limiting formation of T[±] ($\beta_1 = 0.1-0.3$) and breakdown of T[±] ($\beta_2 = 0.8-1.0$) in the reactions of pyridines and SAA with alkyl aryl carbonates,^{2.3} QUIN and SAA with diaryl carbonates,^{5.6} SAA and pyridines with thiolacetates,^{7.11} and SAA with diaryl thionocarbonates.¹³

It is noteworthy that similar values are exhibited by the parameters β_1 , β_2 , and pK_a^0 of the Brönsted equation for the reactions of SAA with CIPNPC and MPNPC. In fact, the values of β_1 and β_2 are the same and the pK_a^0 values differ by 0.1 pK_a unit. The plot (not shown) of log k_N for the reactions of SAA with CIPNPC against log k_N for those of the same amines with MPNPC is linear, according to eq 5 (n = 6; $R^2 = 0.998$).

$$\log k_{\rm N}$$
 (ClPNPC) = 1.04 $\log k_{\rm N}$ (MPNPC) + 0.22 (5)

The larger k_1 values for the reactions of SAA with s of ClPNPC compared to those for the reactions of the same amines with MPNPC could be due to the greater electron withdrawal, including both *inductive* and *resonance* effects, of 4-chloro than 4-methyl on the nonleaving group of the substrate, which would destabilize the ground state of the chloro derivative relative to that with methyl.¹⁷

these two substrates with QUIN.

With the $k_{\rm N}$ values found for the reactions of SAA (excluding piperidine, for which formation of T[±] is rate limiting) with MPNPC and CIPNPC, the corrected p $K_{\rm a}$ values of the nucleophiles, and the p $K_{\rm a}$ values of the nonleaving groups (10.1 and 9.4 for 4-methylphenol and 4-chlorophenol in water, respectively), eq 6 can be deduced by regression analysis (n = 10, $R^2 = 0.982$). In this expression, N and nlg refer to the nucleophile and the nonleaving group, respectively; the p $K_{\rm a}$ (N) and p $K_{\rm a}$ -(nlg) coefficients ($\beta_{\rm N}$ and $\beta_{\rm nlg}$, respectively) are subjected to an error of ± 0.1 and ± 0.2, respectively.

Assuming unity slope and knowing that β_1 and β_2 are

the same for both reaction series, it can be concluded that the reactivity of CIPNPC is ca. 70% greater than that of

MPNPC toward a given SAA amine, and this is mainly reflected in the k_1 values, as found for the reactions of

$$\log k_{\rm N} = -4.75 + 0.90 p K_{\rm a}({\rm N}) - 0.30 p K_{\rm a}({\rm nlg})$$
 (6)

A logarithmic plot (not shown) of the experimental $k_{\rm N}$ vs the calculated one through eq 6 is linear through the origin; the slope is 1.00 ± 0.05 (n = 10, $R^2 = 0.982$).

The values of the coefficients of $pK_a(N)$ and $pK_a(nlg)$ are very similar in eqs 3 and 6, but the constant term in eq 6 (for SAA) is larger than that in eq 3 (for QUIN). This reflects the larger k_N value for the reaction of a given SAA compared to an isobasic QUIN.

The larger k_N value for the reactions of a given substrate with a given SAA relative to those for the reactions with an isobasic QUIN, when breakdown of the zwitterionic tetrahedral intermediate is rate determining, must be attributed to a larger K_1 (= k_1/k_{-1}) value for the SAA reactions since k_2 is independent of the amine basicity and nature.⁵ For the reactions of a series of SAA and QUIN with ethyl (*S*)-(4-nitrophenyl) thiolcarbonate, it was found that QUIN is more reactive toward this substrate than an isobasic SAA when formation of the intermediate is rate determining.¹⁸ This also seems to be true for carbonates.^{3c} Since k_1 is larger for the QUIN

⁽¹⁷⁾ Neuvonen, H.; Neuvonen, K.; Koch, A.; Kleinpeter, E.; Pasanen, P. J. Org. Chem. **2002**, 67, 6995.

The same conclusion can be reached by the following analysis. The fact that the reactions of MPNPC and ClPNPC with QUIN show linear Brönsted plots, whereas the reactions of these substrates with SAA exhibit nonlinear plots, means that the value of the curvature center along the pK_a axis (pK_a^0) is larger for the QUIN reactions. Since it is known that this value is directly related to $\log(k_{-1}/k_2)$, ^{3c,19} it can be concluded that the ratio k_{-1}/k_2 is larger for a given QUIN compared to an isobasic SAA. Since k_2 is independent of the amine basicity and nature,⁵ it follows that k_{-1} should be larger for a given QUIN compared to an isobasic SAA. The same conclusion was reached for the reactions of these two amine series

with ethyl (*S*)-4-nitrophenyl thiolcarbonate¹⁸ and methyl 4-nitrophenyl carbonate in aqueous solution.^{3c}

From the similarity of eqs 2 and 5, an analogous behavior can be expected for the reactions of both substrates with both amine series. A plot (not shown) of log k_N for the reactions of SAA and QUIN with ClPNPC against log k_N for those with MPNPC is linear; the slope is unity (n = 9; $R^2 = 0.996$).

Conclusions

From the results obtained in this work, two conclusions can be drawn. (i) QUIN are better leaving groups from T^{\pm} than isobasic SAA, as found in similar aminolysis. (ii) There is little effect of the nonleaving group basicity on log k_N (β_{nlg}) for these reactions, where β_{nlg} ranges from -0.2 to -0.3, the effect being mainly on k_1 . From these values it is deduced that ClPNPC is ca. 70% more reactive than MPNPC toward SAA and QUIN when expulsion of the leaving group from T^{\pm} is the ratedetermining step.

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