Kinetics and Mechanism of the Aminolysis of Phenyl and 4-Nitrophenyl Chloroformates in Aqueous Solution

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The reactions of secondary alicyclic amines with phenyl and 4-nitrophenyl chloroformates (PClF and NPClF, respectively) are subjected to a kinetic investigation in aqueous solution, 25.0 °C, ionic strength 0.2 (KCl). The reactions are followed spectrophotometrically at 210−270 nm (PClF) and at 310−400 nm (NPClF). Under amine excess, pseudo-first-order rate coefficients (k_{obsd}) are obtained. From linear plots of k_{obsd} vs free amine concentration, the second-order rate coefficients (k_N) for aminolysis are obtained. For the aminolysis of both substrates, linear Brönsted-type plots (log k_N vs amine pK_a) of slopes 0.23 (PClF) and 0.26 (NPClF) are found. The values of the slopes are consistent with stepwise mechanisms where the formation of a zwitterionic tetrahedral intermediate ($T^{\pm}$) is the rate-determining step (k_1 step). In contrast, the aminolysis (anilines) of the same substrates in acetonitrile are concerted, which is attributed to destabilization of $T^{\pm}$ in the latter solvent due to a faster expulsion of the amine from $T^{\pm}$ in acetonitrile compared to water. The values of k_1 are larger for the title reactions compared to the same aminolysis of the corresponding thionochloroformates, and this is attributed to the relatively hard character of these amines which prefer to bind to the harder carbonyl group (relative to thiocarbonyl). There is no change in mechanism by the change of S^- by O^- in $T^{\pm}$, which should destabilize this intermediate. By comparison with the stepwise pyridinolysis of methyl chloroformate, it is concluded that the changes of methoxy by phenoxy (or 4-nitrophenoxy) and a pyridine by an alicyclic amine in $T^{\pm}$ do not greatly affect the stability of these intermediates.

Introduction

Although much attention has been drawn to the kinetics and mechanism of the aminolysis of carboxylic acid derivatives such as esters[1,2] and carbonates,[3,4] the aminolysis reactions of alkyl and aryl chloroformates[5,6] have been less studied kinetically.

It has been found (through a biphasic Brönsted-type plot) that the pyridinolysis of methyl chloroformate in water is stepwise, through the formation of a tetrahedral intermediate ($T^{\pm}$).[5b] In contrast, Lee and co-workers found that the aminolysis of aryl chloroformates in acetonitrile is concerted,[6a] whereas the pyridinolysis of these substrates and methyl chloroformate in the same solvent are stepwise.[6b] On the other hand, the aminolysis (secondary alicyclic amines) of aryl chlorothionoformates in water is a two-stage reaction, whereby the formation of $T^{\pm}$ is the rate-determining step.[7]

To shed more light on the mechanism of the aminolysis of chloroformates and with the aim of clarifying the influence of the amine nature, the solvent, and the electrophilic center of the substrate (CO vs CS) on the mechanism, in the present work we undergo a kinetic study of the reactions of secondary alicyclic amines with phenyl and 4-nitrophenyl chloroformates in water. We will compare our results with those obtained in (i) the pyridinolysis of methyl chloroformate in water,[5b] in order to investigate the effect of the amine nature; (ii) the aminolysis of the same substrates in acetonitrile,[6] to assess the influence of the solvent; and (iii) the aminolysis of the corresponding aryl chlorothionoformates (ArO−CS−Cl) in water,[7] to evaluate the effect of the electrophilic center of the substrate.

Experimental Section

Materials. Phenyl (PClF) and 4-nitrophenyl chloroformates (NPClF) were from Aldrich (99% and 97%, respectively) and used as purchased. Amines were purified as described.[8]

Synthesis of Products. The *O*-phenyl carbamates of piperidine and morpholine (PiPC and MoPC) and the *O*-4-nitrophenyl carbamates of piperidine and morpholine (PiNPC and MoNPC) were synthesized as follows: To a solution of 391 mg (2.5 mmol) of PClF (or 506 mg, 2.5 mmol, of NPClF) dissolved in acetonitrile (10 mL) was added slowly a solution of 425 mg (5 mmol) of piperidine (or 415 mg, 5 mmol, of

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Table 1. Experimental Conditions and k_{obsd} Values for the Aminolysis of Phenyl Chloroformate (PClF)[a]

amine	pH	$10^4[N]_{tot}$,[b] M	10^2k_{obsd}, s^{-1}	no. of runs
piperidine[c]	6.2	30−300	1.63−2.38	7
	6.5	100−500	2.38−4.05	5
	7.0	30−500	1.85−9.24	7
1-(2-hydroxyethyl)	6.0	2.0−4.0	2.74−4.07	5
piperazine[c]	6.3	2.0−4.5	2.83−4.79	6
	6.5	2.0−5.0	2.93−5.47	7
	7.0	2.0−5.0	3.67−7.58	4
	7.3	2.0−5.0	4.48−8.68	4
	7.5	2.0−4.0	4.96−9.08	3
	7.8	2.0−4.0	6.15−12.5	3
morpholine[c]	6.2	2.0−5.0	2.04−2.54	6
	6.5	2.0−5.0	2.29−3.67	7
	7.0	2.0−4.5	4.03−7.38	7
1-(2-hydroxyethyl)-	4.5	2.0−5.0	1.47−2.62	4
piperazinium ion	4.8	2.0−5.0	1.91−3.21	4

[a] In aqueous solution at 25.0 °C, ionic strength is 0.2 M (KCl). [b] Concentration of total amine (free base plus protonated forms). [c] In the presence of 5×10^{-3} M phosphate buffer.

Table 2. Experimental Conditions and k_{obsd} Values for the Aminolysis of 4-Nitrophenyl Chloroformate (NPClF)[a]

amine	pH	$10^4[N]_{tot}$,[b] M	10^2k_{obsd}, s^{-1}	no. of runs
piperidine[c]	6.2	30−300	7.85−10.8	6
	6.5	70−500	4.98−14.9	5
	7.0	30−200	9.15−18.7	5
1-(2-hydroxyethyl)-	6.0	2.0−5.0	11.5−17.4	4
piperazine[c]	6.3	2.0−5.0	14.0−19.1	4
	6.5	2.0−5.0	12.6−18.5	4
	7.0	2.0−5.0	13.5−24.6	4
	7.3	2.0−5.0	14.9−28.3	4
	7.5	2.0−4.0	15.4−35.6	3
	7.8	2.0−4.0	21.2−41.5	3
morpholine[c]	6.2	2.5−4.5	9.29−11.0	5
	6.5	2.0−5.0	10.2−14.1	6
	7.0	2.0−4.5	13.3−20.9	6
piperazinium ion	5.4	2.0−6.0	18.0−49.0	5
	5.5	2.0−6.0	24.8−62.4	5
1-(2-hydroxyethyl)−	4.5	2.0−5.0	8.56−11.1	4
piperazinium ion	4.8	2.0−5.0	9.13−11.9	4

[a] In aqueous solution at 25.0 °C, ionic strength is 0.2 M (KCl). [b] Concentration of total amine (free base plus protonated forms). [c] In the presence of 5×10^{-3} M phosphate buffer.

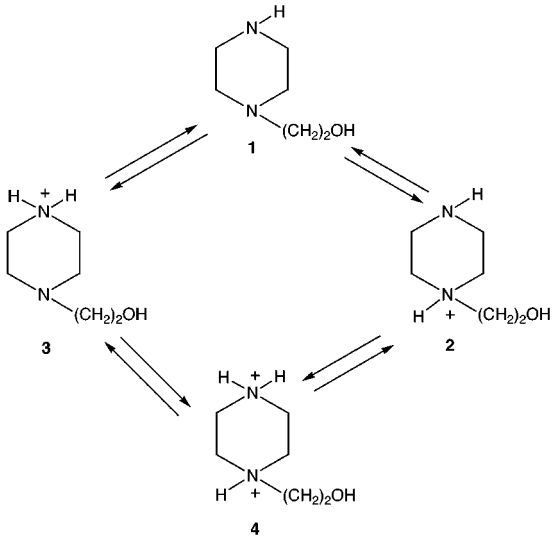
morpholine) in acetonitrile (10 mL). The mixture was left 30 min at ambient temperature. Chloroform (15 mL) was added to this mixture and the solution washed with 10% HCl and water. The organic layer was dried with $MgSO_4$ and filtered under vacuum and the solvent evaporated off. The crystallized products showed the following mp: MoPC 55.1−55.3 °C, PiPC 138.3−138.6 °C, MoNPC 74.9−75.1 °C, and PiNPC 98.2−98.3 °C. The IR, ^{1}H NMR, and ^{13}C NMR spectra were consistent with their structures.

Kinetic Measurements. These were carried out by means of a Hewlett-Packard 8453 diode array spectrophotometer in water, at 25.0 ± 0.1 °C, ionic strength 0.2 M (KCl), and, in some cases, phosphate buffer 0.005 M.

The reactions of PClF were followed in the 210−270 nm range, while the reactions of NPClF were studied at 400 nm (formation of the 4-nitrophenoxide anion), except the reactions with piperazinium and 1-(2-hydroxyethyl)piperazinium ions, which were measured at 310 nm (following the appearance of 4-nitrophenol).

The initial substrate concentration was $(2-5) \times 10^{-5}$ M. All reactions were studied under an excess of amine over the substrate (see below). Pseudo-first-order rate coefficients (k_{obsd}) were found for all reactions; the k_{obsd} values were determined by means of the "infinity" method. The experimental conditions and the k_{obsd} values for these reactions are shown in Tables 1 and 2.

Scheme 1



Product Studies. For the reactions of both substrates with piperidine and morpholine, one of the products was identified as the corresponding carbamate, by comparison of the UV spectra at the end of the reactions with that of an authentic sample of the corresponding carbamate under the same experimental conditions.

In the reactions of NPClF, 4-nitrophenoxide ion was identified as another product (of the parallel hydrolysis); this was achieved by comparison of the UV−vis spectra after completion of the reactions with that of an authentic sample of 4-nitrophenol under the same conditions.

Results and Discussion

The general rate law obtained in the present reactions is given by eqs 1 and 2, where Ar is phenyl or 4-nitrophenyl, k_o and k_N are the rate constants for hydrolysis and aminolysis of the substrates, respectively, and NH represents a secondary alicyclic amine free base.

$$\frac{d[ArS^-]}{dt} = k_{obsd}[ClCOOAr] \quad (1)$$

$$k_{obsd} = k_o + k_N[NH] \quad (2)$$

The second-order rate coefficients for aminolysis (k_N) were obtained as the slopes of plots of eq 2 at constant pH and were pH independent in the reactions of piperidine, morpholine, piperazinium ion, and 1-(2-hydroxyethyl)piperazinium ion. Nevertheless, in the reactions of 1-(2-hydroxyethyl)piperazine in the pH range 6.2−7.8, different straight lines were obtained for each pH, due to the existence of two nucleophiles (species **1** and **2** in Scheme 1) which can react with the substrates. In this case the reaction law obtained is given by eq 3, where k_{N1} and k_{N2} are the second-order rate constants for the reactions of **1** and **2**, respectively, F_1 and F_2 are the corresponding molar fractions, and $[NH]_{tot}$ is the concentration of total amine.[9]

$$k_{obsd} = k_o + (k_{N1}F_1 + k_{N2}F_2)[NH]_{tot} \quad (3)$$

The slopes of the linear plots of k_{obsd} vs $[NH]_{tot}$ at constant pH correspond to k_{Nobsd} of eq 4. Rearrangement of this equation yields eq 5. The k_{N1} and k_{N2} values were

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Table 3. Values of the pK_a of the Conjugate Acids of Secondary Alicyclic Amines and k_N for the Aminolysis of Phenyl Chloroformate (PClF) and 4-Nitrophenyl Chloroformate (NPClF)[a]

		$10^{-4}k_N$, s^{-1} M^{-1}	
amine	pK_a	PCIF	NPCIF
piperidine	11.24	2.61 ± 0.06	8.94 ± 0.3
1-(2-hydroxyethyl)piperizine	9.38	0.87 ± 0.04[b]	2.67 ± 0.2[b]
morpholine	8.78	0.77 ± 0.01	1.68 ± 0.06
1-(2-hydroxyethyl)-piperazinium ion	5.90	0.13 ± 0.01[b] 0.16 ± 0.01[c]	0.34 ± 0.01[b] 0.43 ± 0.04[c]
piperazinium ion	5.81		0.271 ± 0.0001

[a] Values of both pK_a and k_N in aqueous solution, at 25.0 °C; ionic strength is 0.2 M (KCl). [b] Values determined at pH 6.0−7.8 by means of eqs 3−5. [c] Values determined at pH 4.5 and 4.8 by means of eq 2.

obtained as slope and intercept, respectively of linear plots of k_{Nobsd}/F_2 vs F_1/F_2.[9]

$$k_{Nobsd} = k_{N2}F_2 + k_{N1}F_1 \quad (4)$$

$$k_{Nobsd}/F_2 = k_{N2} + k_{N1}F_1/F_2 \quad (5)$$

The hydrolysis rate constants (k_o) for NPClF and PClF are 0.078 ± 0.003 and 0.015 ± 0.002 s^{-1}, respectively, at the pH range studied. The latter value is in agreement with that found in the direct hydrolysis of PClF (0.013 s^{-1}).[10] We also measured the hydrolysis reactions in the absence of amine, and the k_o values obtained were consistent with those found in the aminolysis. In some reactions, the contribution of k_o to the total observed rate constant was more important than the aminolysis term, k_N[NH] in eq 2.

Although neither phenoxide or 4-nitrophenoxide ion are products of the aminolysis reactions, their formation through the parallel hydrolysis reaction allows the determination of the k_{obsd} values and, therefore, the aminolysis rate constants through eq 2 or eqs 3−5.

In some cases the reactions were studied with only a small excess of total amine over the substrate, but due to the presence of the important parallel hydrolysis reaction the pseudo-order condition was maintained, as shown by the good correlation coefficients obtained (greater than 0.999).

The second-order rate coefficients for aminolysis, obtained either by eq 2 or eq 5, together with the pK_a values of the conjugate acids of the amines, are shown in Table 3. With these data (statistically corrected)[9,11] the Brönsted-type plots of Figure 1 were obtained. The slopes of the lines (β) are 0.23 and 0.26 for the aminolysis of PClF and NPClF, respectively. The magnitude of β is in agreement with the values of Brönsted slopes found in stepwise mechanisms of similar reactions when the formation of the zwitterionic tetrahedral intermediate ($T^{\pm}$) is the rate-determining step.[2−4,7−9] For the concerted aminolysis of similar compunds, the values of β are usually in the region 0.5−0.6.[12]

According to the rate law obtained, the analysis of products, and the Brönsted plots, we propose the mechanism shown in Scheme 2 (X = NO_2 or H) for the reactions under scrutiny. Application of the steady-state treatment to $T^{\pm}$ gives $k_N = k_1k_2/(k_{-1} + k_2)$; since the first step is limiting, it follows that in this scheme $k_2 \gg k_{-1}$ and therefore $k_N = k_1$.

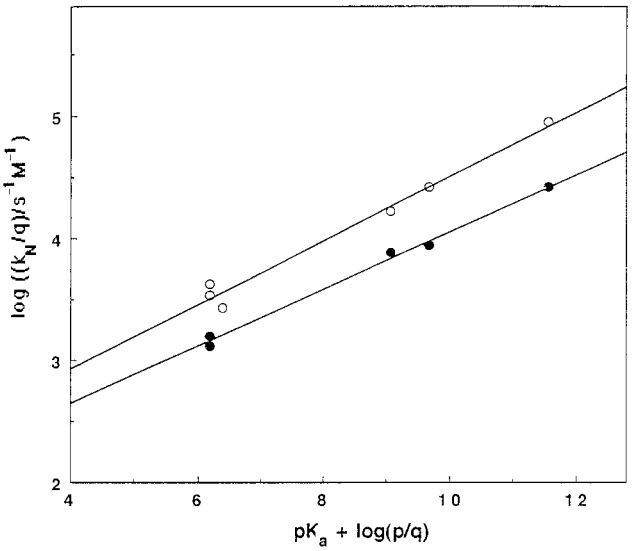
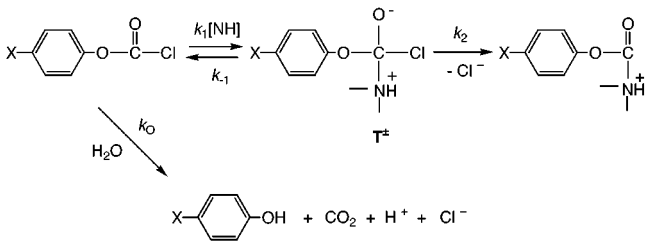


Figure 1. Brönsted-type plots (statistically corrected) obtained in the reactions of secondary alicyclic amines with 4-nitrophenyl (○) and phenyl (●) chloroformates in water, 25.0 °C, ionic strength 0.2 (KCl). The slope values are 0.26 and 0.23, respectively.

Scheme 2



As shown in Table 3, the k_1 values for the aminolysis of NPClF are greater than those of PClF. This is reasonable due to the presence of the powerful electron-withdrawing 4-nitro group in NPClF that leaves the carbonyl group of this substrate more electrophilic than that of PClF.

In contrast to the stepwise aminolysis of aryl chloroformates obtained in this work, Lee and co-workers found that the reactions of anilines with the same substrates in acetonitrile are concerted.[6a] This conclusion was achieved on the basis of a negative value of the cross-correlation coefficient, ρ_{XY} (X and Y are substituents in the amine and the "acyl" group, respectively), and an inverse secondary kinetic isotope effect, $k_H/k_D \approx 0.7-0.9$, involving deuterated aniline nucleophiles.[6a] We have shown that anilines stabilize a tetrahedral intermediate relative to isobasic secondary alicyclic amines.[4e,13] Therefore, it is likely that the reactions of aryl chloroformates with anilines in water be stepwise through the formation of a tetrahedral intermediate ($T^{\pm}$). The destabilization of $T^{\pm}$ in CH_3CN relative to water is in line with the results found in the aminolysis of *S*-aryl *O*-ethyl dithio-

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carbonates: there is a change in mechanism from stepwise (biphasic Brönsted plots and nonlinear plots of k_{obsd} vs amine concentration)[14] to concerted ($\beta = 0.4-0.7$ and $\rho_{XY} = -0.56$)[15] by the change from water to acetonitrile as solvent. Similarly, the aminolysis of 2,4,6-trinitrophenyl *O*-ethyl dithiocarbonate is stepwise (biphasic Brönsted plot) in water[14b] and concerted ($\beta = 0.53$) in a less polar solvent (44 wt % aqueous ethanol).[16] This was attributed to the fact that expulsion of the amine from $T^{\pm}$ (k_{-1} in Scheme 2) should be enhanced in the less polar solvent, while the nucleofugality of the leaving group (k_2) should not change significantly with the solvent nature, rending the intermediate more unstable kinetically in the less polar solvent.[3,7,16]

The k_1 values obtained in this work are ca. 50−100 times greater than those of the same aminolysis of the corresponding thionoformates,[7] showing the greater reactivity of the carbonyl than the thiocarbonyl group of the substrate toward alicyclic amines. This is consistent with the faster attack of these amines to phenyl acetate compared to phenyl thionoacetate.[17] This result has been explained by the harder nature of the carbonyl group relative to thiocarbonyl and the fact that alicyclic amines are considered relatively hard bases.[17,18]

It is known that the change of O^- for S^- in the zwitterionic tetrahedral intermediate makes it less stable due to the superior ability of O^- (relative to S^-) to form a double bond and expel faster both its leaving and amino groups.[19] From this point of view, a destabilized $T^{\pm}$ could be expected in the reaction of aryl chloroformates (relative to aryl chlorothionoformates) as well as a possible concerted mechanism; nevertheless our results show that this destabilizing effect is not great enough as to prevent the existence of the intermediate.

On the other hand, the pyridinolysis of methyl chloroformate in water is stepwise.[5b] The change of methoxy by phenoxy or 4-nitrophenoxy as the "acyl" group of $T^{\pm}$ should stabilize this intermediate;[20,21] in contrast, substitution of a pyridine by a secondary alicyclic amine in $T^{\pm}$ should destabilize it.[3,4e,9,13] Therefore, it is reasonable that these opposing factors partially cancel each other and, as a result, it is likely that these intermediates $T^{\pm}$ be of similar stability and therefore both reactions be stepwise.

The pyridinolysis of aryl chloroformates in acetonitrile is stepwise, with the formation of $T^{\pm}$ rate determining, as shown by a value of $\beta \approx 0.3$.[6b] The fact that the title reactions in water are governed by the same mechanism and limiting step means that the larger value of k_{-1} (see Scheme 2) brought about by the change of a pyridine by a secondary amine in $T^{\pm}$[3,4e,9,13] is counterbalanced by a smaller k_{-1} value resulting from the change of acetonitrile to water.[3,7,16] Since k_2 (Scheme 2) should not be significantly affected either by the amine nature or the solvent,[3,7,16] it is reasonable that for both type of reactions $k_2 \gg k_{-1}$ and the rate-limiting step is the formation of $T^{\pm}$ in both cases.

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(20) It is expected that the values of both k_{-1} and k_2 be smaller for the $T^{\pm}$ formed in the aminolysis of PClF than that in the same aminolysis of methyl chloroformate since the push exerted by PhO from $T^{\pm}$ to expel both the amine and Cl^- should be weaker than that by MeO from the similar intermediate. This is due to the fact that $\sigma_R(PhO) = -0.40$ and $\sigma_R(MeO) = -0.56$,[21] which means that PhO should be less electron donating than MeO from $T^{\pm}$ and therefore the push provided by the former group should be weaker than that by the latter. The same should apply to 4-nitrophenoxy as the "acyl" group of $T^{\pm}$ in view of the stronger electron-withdrawing effect of this group compared to PhO.

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