Concerted Mechanisms of the Reactions of 2,4,6-Trinitrophenyl Methyl Carbonate and 2,4,6-Trinitrophenyl Acetate with Secondary Alicyclic Amines

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Received January 22, 2001

The reactions of secondary alicyclic amines with 2,4,6-trinitrophenyl methyl carbonate (TNPMC) and 2,4,6-trinitrophenyl acetate (TNPA) are subjected to a kinetic study in aqueous solution, 25.0 °C, ionic strength 0.2 (KCl). The reactions are studied by following spectrophotometrically (360 nm) the release of the 2,4,6-trinitrophenoxide anion. Under amine excess, pseudo-first-order rate coefficients (k_{obsd}) are found. Plots of k_{obsd} vs [amine] are linear, with the slope (k_N) independent of pH. The Brönsted-type plots (log k_N vs pK_a of the conjugate acid of the amines) are linear, with slopes $\beta = 0.41$ and $\beta = 0.36$ for the reactions of TNPA and TNPMC, respectively. The predicted breaks of the Brönsted plots for stepwise mechanisms are p$K_a^0 = 6.8$ and 7.3, respectively. The lack of Brönsted breaks for these reactions and the values of the Brönsted slopes are consistent with concerted mechanisms. By comparison of the reactions under investigation among them and with similar aminolysis and pyridinolysis, the following conclusions can be drawn: (i) Secondary alicyclic amines react with TNPA and TNPMC by concerted mechanisms. (ii) TNPA is more reactive toward these amines than TNPMC due to the greater electron release of MeO from the latter substrate. (iii) The change of 2,4-dinitrophenoxy to 2,4,6-trinitrophenoxy in the zwitterionic tetrahedral intermediate ($T^{\pm}$) formed in the reactions of the title amines with 2,4-dinitrophenyl acetate greatly destabilizes $T^{\pm}$. (iv) Secondary alicyclic amines destabilize $T^{\pm}$ relative to pyridines. (v) The intermediate $T^{\pm}$ formed in the reactions of the title amines with *S*-(2,4,6-trinitrophenyl) acetate is greatly destabilized by substitution of *S*-(2,4,6-trinitrophenyl) by *O*-(2,4,6-trinitrophenyl) as the leaving group.

Introduction

The kinetics and mechanisms of the aminolysis of carboxylic acid derivatives such as esters[1−3] and carbonates[4−6] have been extensively investigated. Nevertheless, the mechanisms of the aminolysis of these substrates with very good leaving groups, such as dinitrophenoxide or trinitrophenoxide anions, are not well understood.[3,4,6]

The pyridinolyses of 2,4-dinitrophenyl[3a] and 2,4,6-trinitrophenyl acetates (DNPA and TNPA, respectively),[6b] and 2,4-dinitrophenyl[6a] and 2,4,6-trinitrophenyl methyl carbonates (DNPMC and TNPMC),[6b] have been found to proceed through a zwitterionic tetrahedral intermediate ($T^{\pm}$). These conclusions are based on the biphasic (two linear portions and a curve between) Brönsted-type plots obtained for these reactions. The shape of these plots was explained by a change in the rate-determining step with the variation of the pyridine basicity. For pyridines of low basicity (low pK_a of conjugate acid), decomposition of $T^{\pm}$ to products is rate limiting, whereas for basic pyridines the formation of $T^{\pm}$ is the rate-determining step.[3a,6a,b]

A similar analysis as above can be made for the biphasic Brönsted-type plots obtained in the reactions of secondary alicyclic amines with DNPA,[3c] 2,4-dinitrophenyl and 2,4,6-trinitrophenyl thiolacetates (DNPTA and TNPTA),[7] and quinuclidines (tertiary alicyclic amines) with 2,4-dinitrophenyl and 3,4-dinitrophenyl phenyl carbonates.[4]

On the other hand, the aminolyses (secondary alicyclic amines) of ethyl *S*-(2,4-dinitrophenyl) thiolcarbonate and ethyl *S*-(2,4,6-trinitrophenyl) thiolcarbonate (DNPTC and

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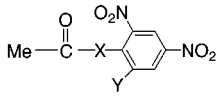
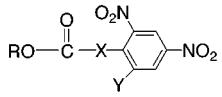
10.1021/jo0100695 CCC: $20.00
Published on Web 08/03/2001

TNPTC) show linear Brönsted plots of slopes β_N ca. 0.48−0.56, which were attributed to concerted mechanisms.[8]

To shed more light on the mechanism of the aminolysis of esters and carbonates, particularly those possessing very good nucleofuges, in the present work we report a kinetic study of the reactions of secondary alicyclic amines with TNPA and TNPMC in water. Comparison of the kinetics and mechanisms of the reactions of both substrates among them allow us to assess the influence of the nonleaving group. Also, we compare the results of this work with those obtained in (i) the pyridinolysis of the same substrates,[6b] in order to investigate the effect of the amine nature; (ii) the same aminolysis of other acetates[3c] and carbonates,[6c] to assess the influence of the basicity of the leaving group; and (iii) the same aminolysis of the corresponding thiolacetate (TNPTA)[7] and thiolcarbonate (TNPTC)[8] in water, to evaluate the effect of the nature of the leaving group.



X = O, Y = H (DNPA)
X = O, Y = NO_2 (TNPA)
X = S, Y = H (DNDTA)
X = S, Y = NO_2 (TNPTA)



R = Me, X = O, Y = H (DNPMC)
R = Me, X = O, Y = NO_2 (TNPMC)
R = Et, X = S, Y = H (DNPTC)
R = Et, X = S, Y = NO_2 (TNPTC)

Experimental Section

Materials. TNPA and TNPMC were synthesized as described[9] and identified by NMR and IR analyses. The amines were purified as reported.[10]

Kinetic Measurements. These were performed spectrophotometrically (Hewlett-Packard 8453 diode array) by following the production of 2,4,6-trinitrophenoxide ion at 360 nm. The reactions were studied under the following conditions: aqueous solution, 25.0 ± 0.1 °C, ionic strength 0.2 (maintained with KCl), initial substrate concentration 5×10^{-5} M, and excess of total amine over the substrate. For the fastest reactions of TNPA, the above spectrophotometer was equipped with a Hi-Tech SFA-20 rapid kinetics stopped-flow accessory.

Pseudo-first-order rate coefficients (k_{obsd}) were found throughout. The experimental conditions of the reactions and the k_{obsd} values obtained are shown in Tables 1 and 2.

Product Studies. 2,4,6-Trinitrophenoxide anion was identified as one of the products of the aminolysis of both substrates, by comparison of the UV−vis spectra after completion of some of these reactions with that of an authentic sample under the same experimental conditions.

Results and Discussion

The kinetic law obtained for all the reactions studied is that described by eq 1, where P is 2,4,6-trinitrophenoxide anion, S represents the substrate, and k_{obsd} is the pseudo-first-order rate coefficient (excess of amine over the substrate was employed in all cases).

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

Plots of k_{obsd} against concentration of total amine ($[N]_{tot}$ = concentration of free amine plus its conjugate acid) at constant pH were linear for all reactions, in accordance to eq 2. In this equation F_N is the free amine fraction,

Table 1. Experimental Conditions and k_{obsd} Values for the Aminolysis of 2,4,6-Trinitrophenyl Methyl Carbonate (TNPMC)[a]

amine	pH	$10^3[N]_{tot}/M^b$	$10^2k_{obsd}/s^{-1}$	no. of runs
piperidine	9.00[c]	1.0−10	0.43−1.7	6
	9.50[c]	1.0−10	1.0−3.5	7
piperazine	8.90	0.40−4.0	0.35−3.3	6
	9.20	0.20−2.0	0.53−3.0	6
1-(2-hydroxyethyl)-piperazine	8.50	0.60−6.0	0.55−4.5	6
	9.08	0.60−6.0	1.3−10	6
	9.38	0.60−6.0	1.8−12	8
morpholine	8.48	1.0−9.0	1.0−8.5	5
	8.78	5.0−9.0	7.4−13	3
	9.08	0.50−6.0	0.95−11	5
1-formylpiperazine	7.68	1.0−10	0.38−3.1	6
	7.98	1.0−10	0.39−4.7	6
	8.28	1.0−10	0.34−7.1	6
piperazinium ion	5.51	1.0−10	0.071−0.73	5
	5.81	1.0−10	0.13−1.2	5
	6.11	1.0−10	0.17−1.4	5

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Concentration of total amine (free base plus protonated forms). [c] In the presence of borate buffer 0.005 M.

Table 2. Experimental Conditions and k_{obsd} Values for the Aminolysis of 2,4,6-Trinitrophenyl Acetate (TNPA)[a]

amine	pH	$10^3[N]_{tot}/M^b$	$10^2k_{obsd}/s^{-1}$	no. of runs
piperidine	6.70[c]	2.0−150	0. 33−0.87	7
	7.00[c]	2.0−100	0.42−0.92	6
	7.30[c]	2.0−80	0.36−0.68	5
1-(2-hydroxyethyl)-piperazine	8.50[d]	0.60−6.0	3.1 − 24	6
	9.08[d]	0.60−6.0	5.5−51	6
	9.38[d]	0.60−6.0	8.3−94	6
morpholine	4.50[e]	2.0−60	0.33−0.42	6
	4.80[e]	2.0−120	0.34−0.59	6
	5.10[e]	2.0−60	0.34−0.64	8
1-formylpiperazine	4.50[e]	0.50−10	0.34−0.37	6
	5.00[e]	0.50−5.0	0.34−0.39	6
	5.50[e]	0.50−5.0	0.35−0.49	6
piperazinium ion	5.51	1.0−10	0. 71−2.6	7
	5.81	1.0−10	0.70−3.8	7
1-(2-hydroxyethyl)-piperazinium ion	4.60	10−100	0.54−3.0	7
	4.80	10−100	0.65−4.3	6

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Concentration of total amine (free base plus protonated forms). [c] In the presence of phosphate buffer 0.005 M. [d] A stopped-flow accessory was used to follow these reactions. [e] In the presence of citrate buffer 0.005 M.

and k_0 and k_N are the rate coefficients for hydrolysis and aminolysis of the substrates, respectively. The values of k_N were obtained by dividing the slopes of k_{obsd} vs $[N]_{tot}$ plots by F_N; these k_N values, as well as the k_o values, were found to be pH independent over the pH range studied. Therefore, the definitive k_N values were obtained as the slopes of plots of k_{obsd} vs [NH] (eq 3), where NH is the free amine, using several pH values in a single plot.

$$k_{obsd} = k_0 + k_N F_N [N]_{tot} \quad (2)$$

$$k_{obsd} = k_0 + k_N [NH] \quad (3)$$

The values of k_N together with those of the pK_a of the conjugate acids of the amines were statistically corrected with $p = 2$ and $q = 1$, except piperazinium ion with $p = 4$ and piperazine with $q = 2$.[10,11] These corrected values are shown in Table 3.

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Table 3. Statistically Corrected Values of pK_a for Conjugate Acids of Amines and k_N for the Aminolysis of TNPMC and TNPA[a]

amine	pK_a + log(p/q)	$k_{Nq}^{-1}/s^{-1}M^{-1}$ TNPMC	$k_{Nq}^{-1}/s^{-1}M^{-1}$ TNPA
piperidine	11.54	150 ± 6	992 ± 67
piperazine	9.94	48 ± 3	–
1-(2-hydroxyethyl)-piperazine	9.68	50 ± 2	293 ± 11
morpholine	9.08	29 ± 1	237 ± 10
1-formylpiperazine	8.28	10.6 ± 0,6	86 ± 5
piperazinium ion	6.41	2.3 ± 0.1	7.5 ± 0.5
1-(2-hydroxyethyl)-piperazinium ion	6.20	–	9.1 ± 0.5

[a] Both pK_a and k_N values in aqueous solution, 25.0 °C, ionic strength 0.2 (KCl). These values are statistically corrected with $p = 2$ and $q = 1$, except piperazine with $q = 2$ and piperazinium ion with $p = 4$ (see text).

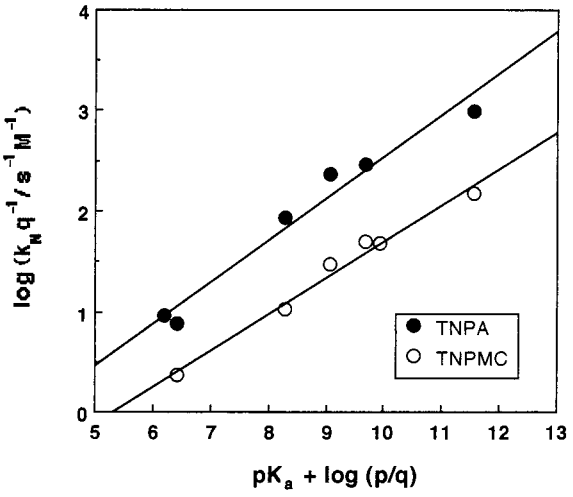


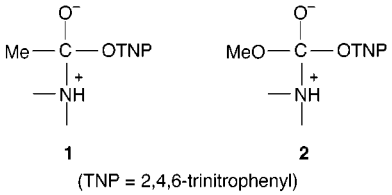
Figure 1. Brönsted-type plots (statistically corrected) obtained in the reactions of secondary alicyclic amines with 2,4,6-trinitrophenyl acetate (TNPA) and 2,4,6-trinitrophenyl methyl carbonate (TNPMC) in aqueous solution, 25.0 °C, ionic strength 0.2 M (KCl). The slopes (β) are 0.41 and 0.36, respectively.

With the data of Table 3 the Brönsted-type plots of Figure 1 were obtained. The plots are linear, with slopes $\beta = 0.41 \pm 0.05$, and $\beta = 0.36 \pm 0.05$, for the reactions of TNPA and TNPMC, respectively.

These values are in accord with a concerted process where the structure of the transition state remains constant with the variation of the nucleophile basicity.[12] These β values are in agreement with those found in the concerted reactions of secondary alicyclic amines with DNPTC and TNPTC.[8] The concerted nature of these reactions was deduced by the linear Brönsted plots obtained, with slopes $\beta = 0.56$ and 0.48, respectively,[8] together with the fact that the predicted Brönsted breaks, had these reactions been stepwise, were not observed.[8] These β values are also in agreement with that obtained in the concerted pyridinolysis of *N*-methoxycarbonylisoquinolinium ion, where a linear Brönsted relationship of slope $\beta = 0.58$ was observed over a range of pK_a greater than and less than that of isoquinoline.[13] The Brönsted slopes obtained in this work are also in accordance with those found in the concerted reactions of TNPTC with anilines ($\beta = 0.54$)[14] and those of quinuclidines with DNPTC and TNPTC ($\beta = 0.54$ and 0.47, respectively).[15]

The β value alone is not sufficient to prove that a reaction is concerted; one must be sure that the hypothetical break of the Brönsted-type plot (due to the change in the rate-determining step of a stepwise process) is located at a pK_a value within the pK_a range of the nucleophiles used in the plot.[8,16]

To find the hypothetical Brönsted breaks (pK_a^0) of the reactions under investigation, the following analysis can be made. The stepwise reactions of DNPA with secondary alicyclic amines[3c] and pyridines[3a] show Brönsted breaks at pK_a = pK_a^0 = 9.1 and 7.3, respectively. Namely, there is a pK_a^0 increase of ca. 1.8 units in going from pyridines to secondary alicyclic amines. Since the stepwise pyridinolysis of TNPA exhibits a pK_a^0 value of 5.0,[6b] a pK_a^0 value of ca. 6.8 can be deduced for the reactions of the secondary amines with TNPA. As can be seen in Figure 1, there is no break in the Brönsted plot for TNPA, which covers a pK_a range 5.0−9.1. The lack of a Brönsted break precludes the stepwise mechanism, which together with the fact that the Brönsted plot is linear with slope $\beta = 0.41$ indicates that the reactions of TNPA with the secondary amines are concerted. This means that the zwitterionic tetrahedral intermediate **1** either exists but it is very unstable or it is too unstable to exist; in the latter case the mechanism is called enforced concerted.[12]



1 **2**

(TNP = 2,4,6-trinitrophenyl)

On the other hand, the stepwise pyridinolyses of DNPA and DNPMC show Brönsted breaks of pK_a^0 = 7.3 and 7.8, respectively;[3a,6a] i.e., there is a pK_a^0 increase of ca. 0.5 pK_a unit in going from acetate to methyl carbonate. Therefore, the predicted Brönsted break for the reactions of secondary alicyclic amines with TNPMC would be pK_a^0 = 6.8 + 0,5 = 7.3. There is no such a break, as seen in Figure 1. This result and the fact that the Brönsted slope is $\beta = 0.36$ allows us to conclude that the reactions of secondary alicyclic amines with TNPMC are also concerted.

It is known that the change of methyl to methoxy or ethoxy in a tetrahedral intermediate destabilizes it. Examples of this destabilization are (i) the stepwise acetyl transfer[17] in contrast to the concerted methoycarbonyl transfer[13] between pyridines; (ii) the facts that the aminolyses (secondary alicyclic amines) of DNPTA and TNPTA are stepwise,[7] whereas the same aminolysis of the corresponding ethyl carbonates (DNPTC and TNPTC) are concerted;[8] (iii) the faster expulsion rates of both the nucleophile and the nucleofuge from the tetrahedral intermediate with ethoxy compared to that with methyl.[18] For these reasons it is reasonable that the aminolysis of TNPMC be concerted in view that the putative tetrahe-

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dral intermediate (**2**) would be more unstable than that formed in the same reactions with TNPA (intermediate **1**).

The higher reactivity of TNPA than TNPMC toward secondary alicyclic amines (see Figure 1) is in accord with the results found in stepwise aminolyses. The pyridinolyses of 4-nitrophenyl acetate,[19] DNPA,[3a] and TNPA[6b] are faster than those of 4-nitrophenyl methyl carbonate,[5a] DNPMC,[6a] and TNPMC,[6b] respectively. The same is true for the reactions of secondary alicyclic amines with DNPA[3c] and DNPMC.[6c] The greater reactivity of acetates compared to the corresponding methyl carbonates has been explained by the larger electron-releasing effect of the MeO group in the carbonate, relative to Me in the acetate, rendering the former carbonyl carbon less positively charged and, therefore, less susceptible to amine attack.[5a] This should equally apply to stepwise as well as concerted mechanisms.

The fact that the reactions of TNPA and TNPMC with pyridines are stepwise,[6b] while those of the same substrates with alicyclic amines are concerted (this work), indicates that the zwitterionic tetrahedral intermediate formed in the former reactions is destabilized by substitution of a pyridine by a secondary alicyclic amine. This is in line with previous findings. The reactions of secondary alicyclic amines with DNPTC,[8a] TNPTC,[8b] and bis-4-nitrophenyl thionocarbonate are concerted,[20] while the pyridinolyses of these substrates are stepwise.[20,21]

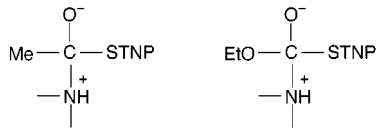
The high instability of the putative tetrahedral intermediate ($T^{\pm}$) formed with the alicyclic amines has been associated to a large nucleofugality rate of these amines from the intermediate. Pyridines are known to leave $T^{\pm}$ slower than isobasic alicyclic amines. Therefore, substitution of an alicyclic amine by an isobasic pyridine in $T^{\pm}$ stabilizes kinetically the latter species.[21]

On the other hand, the reactions of DNPA[3c] and DNPMC[6c] with secondary alicyclic amines are stepwise while those of TNPA and TNPMC with the same amines are concerted (this work). The higher instabilities of the zwitterionic intermediates formed in the latter reactions (intermediates **1** and **2**) should be due to the greater nucleofugality from **1** or **2** of 2,4,6-trinitrophenoxide compared to 2,4-dinitrophenoxide. These results are in line with the facts that the reactions of anilines with DNPTC are stepwise whereas the same reactions of TNPTC are concerted.[14] The change in mechanism with the introduction of a nitro substituent in the leaving group has also been observed in the reactions of alicyclic amines with NPTC (stepwise)[22] and DNPTC (concerted),[8a] and in the reactions of quinuclidines with NPTC (stepwise) and DNPTC (concerted).[15]

The reactions of secondary alicyclic amines with TNPTA proceed through the formation of a zwitterionic tetrahedral intermediate (**3**).[7] In contrast, the reactions of the same amines with TNPA are driven by a concerted mechanism (this work). This means that the intermediate **3** is greatly destabilized by substitution of *S*-2,4,6-trinitrophenyl by *O*-2,4,6-trinitrophenyl as the leaving group to yield **1**. This destabilization is reasonable in terms of the similar basicities of these nucleofuges (pK_a 1.4 and 0.3 in water at 25 °C)[7,23] and the fact that aryl oxides are better nucleofuges than isobasic benzenethiolates.[24] This in agreement with the reports on the stabilization of tetrahedral intermediates caused by the change of *O*-groups to *S*-groups in the central carbon atom.[25]

A reviewer has pointed out that the above change has the opposite effect in the aminolysis of 2,4-dinitrophenyl alkyl carbonates. In fact the reactions of secondary alicyclic amines with DNPTC are concerted[8a] whereas the same aminolysis of DNPMC is stepwise.[6c] Assuming the effects of EtO and MeO in a zwitterionic tetrahedral intermediate ($T^{\pm}$) are the same,[26] this means that substitution of DNPS (DNP = 2,4-dinitrophenyl) in $T^{\pm}$ by DNPO *stabilizes* the intermediate $T^{\pm}$, in contrast to the effect of this change in the trinitrophenyl acetate derivatives. Nevertheless, it should be taken into account that DNPO is *more basic* than DNPS (pK_a of DNPOH and DNPSH = 4.0 and 3.4, respectively)[7,23] and perhaps a worse leaving group than DNPS, despite the fact that ArO are better nucleofuges than isobasic ArS.[24]

On the other hand, there is no change in mechanism by the above substituents change in the reactions of the same amines with the corresponding carbonates, TNPTC and TNPMC (both reactions are concerted). This is because the tetrahedral intermediate (**4**) possessing the groups *S*-2,4,6-trinitrophenyl and EtO is already very unstable or nonexistent.[8b] It is known that EtO or MeO destabilizes a tetrahedral intermediate relative to Me, as discussed above.



3 **4**

(TNP = 2,4,6-trinitrophenyl)

TNPTC is less reactive[8b] than TNPMC (this work) toward secondary alicyclic amines. This is in line with the findings in other aminolyses: the pyridinolyses of 4-nitrophenyl methyl carbonate,[5a] DNPMC,[6a] and TNPMC[6b] are faster than the reactions of the same amines with the corresponding *S*-aryl ethyl thiolcarbonates.[21] Also in agreement are the faster reactions of anilines with DNPMC[6c] compared to DNPTC.[14] The higher reactivity of carbonates than thiolcarbonates can be ascribed to steric inhibition to amine attack by the sulfur atom in thiolcarbonates relative to the oxygen atom in carbonates.

Acknowledgment. The financial assistance given to this work by FONDECYT of Chile (project 1960460) is gratefully acknowledged.

JO0100695

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