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RESEARCH ARTICLE

Theoretical studies on the relative reactivities of aryl thiol, thiono and dithio carbonates and carbamates

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RHF, MP2 and DFT calculations were carried out for the unhydrated and explicitly solvated (by five water molecules) putative zwitterionic complexes formed in the aminolysis of oxo {(O, O)} and thio {(O, S), (S, O) and (S, S)} carbonates [MeO–C(=Y)–Y'Ar] and carbamates [NH₂–C(=Y)–Y'Ar, where Y and Y' are O or S] with ammonia. The reorganization energy of the carbonyl carbon from an sp² to an sp³ center, *i.e.*, the energy needed to form a zwitterionic tetrahedral intermediate, was inversely related to the experimental rate of the aminolysis of carbonates as Y and Y' are varied, (O, S) < (O, O) < (S, S) < (S, O). For carbamates the reorganization energy is the highest and the solvation energy is the lowest among ester, carbonate and carbamate series, which is suggestive of the difficulty of zwitterionic intermediate formation and changeover to a concerted mechanism found experimentally for the aminolysis of the carbamates.

Keywords: DFT studies; Carbonates; Carbamates; Zwitterionic intermediates; Aminolysis

1. Introduction

The aminolysis of aryl thiol, thiono and dithio esters, carbonates and carbamates, **1–3**, where Y, Y'=O or S, and R=H, alkyl, aryl or arylalkyl group, has been a subject of numerous experimental [1–8] and theoretical studies [9–14] because of the importance of this process in chemistry and biochemistry. It has been shown that there are five factors that influence the



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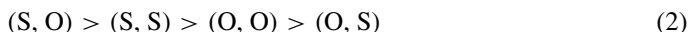
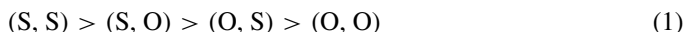


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aminolysis mechanisms of **1–3**: (i) The push provided by a non-leaving group, R, RO or RNH, [1–3] (ii) the nucleofugality of amine from a putative zwitterionic tetrahedral intermediate, T[±], [3, 4] (iii) the polarity of solvent [15], (iv) the atom pair Y and Y' [16, 17] and (v) the

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nucleofugality of the leaving group, Y'Ar [18]. Experimentally, the rate of aminolysis of esters with secondary alicyclic amines in water is found to decrease in the order dithio > thiono > thiol (rate order (1)), whereas for carbonate series the rate of thiono becomes faster than that of dithio compound following rate order (2) [16, 17].

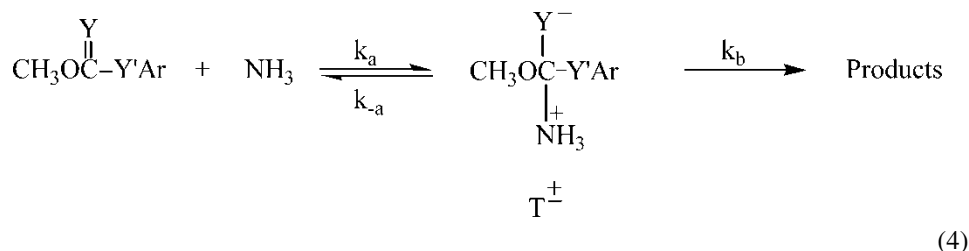


It has been shown that the main factor determining the rate order of the ester aminolysis, rate order (1), is the strong vicinal charge transfer interaction between a π type non-bonding orbital on Y' and a vacant π^* orbital of C=Y, $n_{Y'} \rightarrow \pi_{C=Y}^*$ [19]. This type of interaction becomes stronger with the thio carbonyl group (lower $\pi_{C=S}^*$ level) and thiol sulfur (higher π -type lone pair level), relative to the corresponding oxygen analogs due to a narrower energy gap between the two interacting

$$SE = -\Delta E^{(2)} = \frac{2(F_{ij})^2}{\delta\varepsilon_{ij}} \quad (3)$$

orbitals [$\delta\varepsilon_{ij}$ in equation (3)]. The pattern of variation in stabilization energy, ΔSE , in stabilizing interaction, which is represented by a second order perturbation energy [20, 21], equation (3) (where i, j = interacting orbitals, F_{ij} a Fock matrix element that is proportional to the overlap integral, S_{ij} , and $\delta\varepsilon_{ij} = \varepsilon_i - \varepsilon_j$), is in this case set by the pattern of variations in the energy gap $\Delta\delta\varepsilon_{n\pi^*}$ [19, 21].

In this work, we carried out *ab initio* and DFT studies to investigate possible causes of the rate order change depending on Y, Y'=O or S found experimentally from that of rate orders (1) to (2), as we changed from the aminolysis of esters to that of the corresponding carbonates, equation 4. Steady-state approximation for a stepwise process



in which breakdown of the intermediate, T^\pm , is rate-limiting leads to the overall rate $k_2 = (k_a/k_{-a})k_b = Kk_b$. We adopted the procedure of calculating the stability and structure of the putative zwitterionic intermediates (T^\pm) solvated explicitly by up to five water molecules (Z_{5w}), since the aminolysis of these, esters and carbonates, is known to proceed mainly stepwise through a zwitterionic intermediate, T^\pm [1–8]. We have also extended the study to an additional system, carbamates **3**, which have been shown to react concertedly in the aminolysis [16]. The putative zwitterionic intermediates are so unstable that they cannot exist in the aminolysis of carbamates.

2. Calculations

The computations were carried out with the *Gaussian 03* program package [22]. Minimum energy structures of the zwitterionic complexes solvated explicitly by zero and five water molecules (Z_{nw} , $n = 0$ and 5) were located initially using the AM 1 method, which were

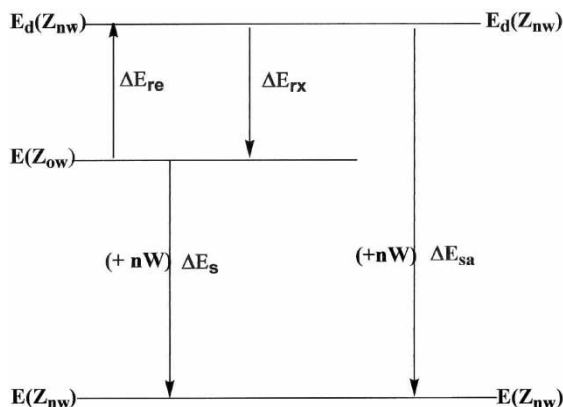


Figure 1. Energy changes scheme.

then fully optimized by applying the following theory/basis sets [9, 19]: RHF/6-31G**, B3LYP/6-31G**, and MP2/6-31G**. Single point calculations were additionally performed at the B3LYP/6-311 + G**//B3LYP/6-31G** level. Analytical harmonic vibrational frequencies were computed at the first two levels to characterize the nature of the structures. We used the electronic energies uncorrected for entropy changes, as in the previous works [9, 19], since the entropies tend to be less accurate due to the presence of many low-lying frequencies in the water clusters [19, 23]. For comparisons of the stability of zwitterions, we used the following three quantities: reorganization energy ΔE_{re} , the energy acquired from explicit solvation by water ($n = 5$) molecules to rehybridize the carbonyl carbon center from sp^2 to sp^3 (this is really the energy needed to form a zwitterionic tetrahedral intermediate in water), solvation energy ΔE_s of stabilization and solvent assistance ΔE_{sa} , which are the total energy provided by the solvating water molecules, as defined by equations 5–7. Here, Z_{nw} is a zwitterion solvated explicitly by n water molecules, $E_d(Z_{nw})$ is the energy for Z_{nw} without all the water molecules and leaving it unrelaxed, and ΔE_{rx} is the relaxation energy.

$$\Delta E_{re} = E_d(Z_{nw}) - E(Z_{0w}) = -\Delta E_{rx} \quad (5)$$

$$\Delta E_s = E(Z_{nw}) - [E(Z_{0w}) + nE(H_2O)] \quad (6)$$

$$\Delta E_{sa} = \Delta E_s + (-\Delta E_{re}) = \Delta E_s + \Delta E_{rx} \quad (7)$$

The energy changes are schematically shown in figure 1.

Natural bond orbital (NBO) analyses [20] were carried out on the $CH_3OC(=Y)Y'H$ and $NH_2C(=Y)Y'H$ systems for $Y, Y' = O$ or S at the RHF/6-31 + G* level.

3. Results and discussion

3.1 Carbonates

The calculated energies for zero- (Z_{0w}) and penta-hydrated zwitterions (Z_{5w}) at the three levels plus at the B3LYP/6-311 + G**/B3LYP/6-31G** level are summarized in the Supplementary material. The unhydrated, gas-phase, zwitterions have a loosely complexed structure in which an ammonia molecule is attached to carbonates maintaining the sp^2 hybridized carbonyl carbon center (C_1), as reported previously for the ester series [9, 19]. The length of C–N bond (d_{14}) has been shown to provide the most sensitive indicator of the hybridization state of the carbonyl

group [9]; thus, for Z_{0w} with sp^2 state d_{14} was long, ranging from 3.56 to 3.85 Å ($\Delta d_{14} \approx 0.3$ Å), whereas for Z_{5w} with sp^3 state it was shorter, ranging from 1.53 to 1.58 Å ($\Delta d_{14} \approx 0.03$ Å), both decreasing in the reverse of rate order (2), *i.e.*, the shorter the d_{14} , the greater is the stability of Z_{0w} as well as Z_{5w} . Thus, it seems reasonable to expect that the shorter the d_{14} , the smaller will be the Δd_{14} ($=d_{14}(0w) - d_{14}(5w)$), and hence the reorganization energy, ΔE_{re} , and the easier will be the formation of zwitterionic intermediates with a larger k_a (in equation 4). Since $\Delta E_{re} = -\Delta E_{ex}$ (figure 1), a smaller positive ΔE_{re} (a larger k_a) will give a smaller negative ΔE_{rx} (a smaller k_{-a}) and will result in a larger equilibrium constant $K = k_a/k_{-a}$ in equation 4. Experimentally, it was found that when k_a is large, K becomes large, and the overall rate, k_2 , also becomes larger in the stepwise aminolysis of esters with various atom pairs $Y, Y'=O$ or S , albeit k_2 is given by Kk_b (equation 4) [19]. The penta-hydrated zwitterionic tetrahedral intermediates are structurally similar, irrespective of the atom pairs, Y and Y' , with five water molecules forming altogether nine hydrogen bonds in three cyclic hydrogen bond ring networks, terminating at the negatively charged Y^- and one of the three hydrogens on the cationic ammonium nitrogen atom, and the two cyclic rings are also interconnected by a hydrogen bond bridge. General pattern of Z_{5w} structures is quite similar for all the penta-hydrated zwitterions of carbonates, as shown in figure 2 for the dithio carbonate. The calculated reorganization energies, ΔE_{re} , solvation energies, ΔE_s , and solvent assistance, ΔE_{sa} , are presented in tables 1–3.

We note in table 1 that the reorganization energy, ΔE_{re} , irrespective of the method used, increases in the order of decreasing experimental rate as given by sequence (2). This means that the easier the formation of a zwitterionic intermediate (with a smaller ΔE_{re}), the faster is the overall aminolysis rate (with a larger $k_2 = Kk_b$). This rate order (2) of the aminolysis in water for the carbonate series differs, however, from (1) for the ester series [16]. The magnitude of ΔE_{re} value is known to vary primarily with the SE (equation 3) gained by the

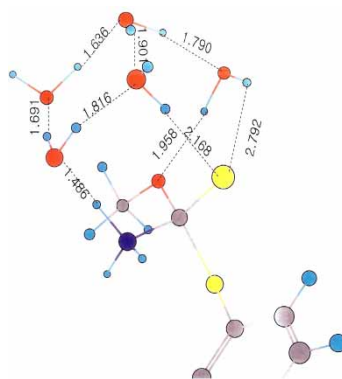


Figure 2. The B3LYP/6-31G** Z_{5w} structure for carbonate (S, S) (benzene ring is shown partly). Bond lengths are in Å.

Table 1. The reorganization energies (ΔE_{re} in kJ/mol) at various levels of theory for Z_{5w} of carbonates, $CH_3OC(=Y)-Y'Ar$, with $Y, Y'=O$ or S .

Y, Y'	O, O	O, S	S, O	S, S
RHF/6-31G**	192.8	210.2	130.3	144.6
B3LYP/6-31G**	169.7	176.8	144.6	157.2
B3LYP/6-311 + G**//	166.4	173.4	148.9	164.1
B3LYP/6-31G**				

Table 2. The solvation energies (ΔE_s in kJ/mol) at various levels of theory for Z_{5w} of carbonates, $\text{CH}_3\text{OC}(=\text{Y})-\text{Y}'\text{Ar}$, with $\text{Y}, \text{Y}'=\text{O}$ or S .

Y, Y'	O, O	O, S	S, O	S, S
RHF/6-31G**	-110.0	-89.6	-134.6	-123.6
B3LYP/6-31G**	-238.5	-223.1	-233.6	-223.5
B3LYP/6-311 + G**//	-132.2	-113.6	-132.3	-116.3
B3LYP/6-31G**				

Table 3. The solvent assistance (ΔE_{sa} in kJ/mol) at various levels of theory for Z_{5w} of carbonates, $\text{CH}_3\text{OC}(=\text{Y})-\text{Y}'\text{Ar}$, with $\text{Y}, \text{Y}'=\text{O}$ or S .

Y, Y'	O, O	O, S	S, O	S, S
RHF/6-31G**	-302.8	-299.7	-264.9	-268.2
B3LYP/6-31G**	-408.2	-399.9	-378.1	-380.7
B3LYP/6-311 + G**//	-298.6	-287.1	-281.2	-280.5
B3LYP/6-31G**				

vicinal $n_{\text{Y}'} \rightarrow \pi_{\text{C}=\text{Y}}^*$ charge transfer interactions as we vary the atom pair Y, Y' [19]. There are two factors that determine the pattern of variation in the stabilization energy of vicinal charge transfer interaction, ΔSE , *i.e.*, $\Delta \delta \varepsilon_{ij}$ and ΔF_{ij} in equation 3 [21] and it has been shown that for the ester series the ΔSE is controlled by the former, the variation of energy gap [19]. This leaves a possibility of pattern (of ΔSE) set by the latter, the variation of F_{ij} , for the different rate order of the carbonate series. The pattern of ΔSE will be set by ΔF_{ij} when the energy gaps ($\delta \varepsilon_{ij}$) are relatively large, and in such cases F_{ij} values are larger for an oxygen atom ($\text{Y}'=\text{O}$) than that of a sulfur atom ($\text{Y}'=\text{S}$) in the $n_{\text{Y}'} \rightarrow \pi_{\text{C}=\text{Y}}^*$ interaction. As a result, the electron donor ability of O becomes larger than S and the stabilization energy for the Y, O pair becomes larger than that for the Y, S pair ($\text{Y}=\text{O}$ or S) [21] leading to the rate order change from rate orders (1) to (2), in agreement with the experimental rate orders. The results of our NBO analyses have indeed shown that the pattern of ΔSE values for both the $n_{\text{Y}'} \rightarrow \pi_{\text{C}=\text{Y}}^*$ and $n_{\text{O}} \rightarrow \pi_{\text{C}=\text{Y}}^*$ (O is the methoxy oxygen) vicinal charge transfer interactions in the carbonates are set by ΔF_{ij} (not by $\Delta \delta \varepsilon_{ij}$), table 4. We note that carbonates (and also carbamates) with $\text{Y}'=\text{O}$ have larger F_{ij} as well as $\delta \varepsilon_{ij}$ values relative to those with $\text{Y}'=\text{S}$, but the SE values are larger due to the larger F_{ij} , *i.e.*, ΔF_{ij} determines ΔSE . In the carbonates the methoxy oxygen atom donates π electrons to the $\pi_{\text{C}=\text{Y}}^*$ orbital and as a result the $\text{C}=\text{Y}$ π bond stretches [20, 21, 24] so that the $n_{\text{Y}'} \rightarrow \pi_{\text{C}=\text{Y}}^*$ interaction becomes weaker than that for the esters for which there is no extra non-bonding orbitals to donate π electrons to $\pi_{\text{C}=\text{Y}}^*$.

Table 4. The NBO analysis of SE ($= -2F_{ij}^2/\delta \varepsilon_{ij}$) involved in the $n_{\text{Y}'} \rightarrow \pi_{\text{C}=\text{Y}}^*$ interactions in carbonates ($\text{MeOC}(=\text{Y})-\text{Y}'\text{H}$) and carbamates ($\text{NH}_2\text{C}(=\text{Y})-\text{Y}'\text{H}$) at the RHF/6-31 + G* level.

		SE (kJ/mol)	$\delta \varepsilon_{ij}$ (a.u)	F_{ij} (a.u)
O, O	carbonate	-250.5	0.73	0.193
	carbamate	-241.8	0.72	0.190
O, S	carbonate	-140.2	0.57	0.127
	carbamate	-134.4	0.56	0.125
S, O	carbonate	-308.4	0.60	0.196
	carbamate	-295.1	0.58	0.193
S, S	carbonate	-194.3	0.43	0.132
	carbamate	-185.0	0.42	0.130

Table 5. The NBO analysis of vicinal charge transfer interaction energies, SE (equation 3) in kJ/mol, in carbonates (MeOC(=Y)-Y'H) and carbamates (NH₂C(=Y)-Y'H) at the RHF/6-31 + G* level.

Y, Y'	O, O	O, S	S, O	S, S
MeO ₅ - C ₁ (=Y) - Y' ₃ H				
$n_{O5} \rightarrow \pi_{C=Y}^*$	-287.1	-277.7	-366.7	-331.3
$n_{Y'3} \rightarrow \pi_{C=Y}^*$	-250.5	-140.2	-308.4	-194.3
NH ₂ - C(=Y) - Y'H				
$n_N \rightarrow \pi_{C=Y}^*$	-364.4	-371.5	-512.3	-501.3
$n_{Y'} \rightarrow \pi_{C=Y}^*$	-241.8	-134.4	-295.1	-185.0

This trend holds also for the carbamates where N (NH₂) serves as a donor. But in this case the effect of $n_N \rightarrow \pi_{C=Y}^*$ interaction on $n_{Y'} \rightarrow \pi_{C=Y}^*$ is greater than the effect of the $n_O \rightarrow \pi_{C=Y}^*$ interaction on $n_{Y'} \rightarrow \pi_{C=Y}^*$ in the carbonates and π (C=Y) bond elongation is greater than that by O (CH₃O) in the carbonates [25, 26]. As a result, $n_{Y'} \rightarrow \pi_{C=Y}^*$ interaction weakens more with a greater decrease in the SE value, table 5.

The solvation energies, ΔE_s , in table 2 represent the stabilization energy of zwitterions Z_{5w} gained by hydrogen bonding by five water molecules, which form altogether nine hydrogen bonds. Thus, the average H-bond energy per hydrogen bond, $\Delta E_s/9$, is ca -12.6–-14.6 kJ/mol (at the B3LYP/6-311 + G**//B3LYP/6-31G** level), which is somewhat less than the Hartree–Fock limit for a water dimer complexation energy of -17.2 kJ/mol [20]. The ΔE_s values do not follow the order rate (2) in general except those by the RHF results. However, in all cases the ΔE_s values are larger negative for Y'=O than the corresponding values for Y'=S in the Y, Y' pair. This is due to a greater increase in the negative charge on the anionic Y atom in the penta-hydrated zwitterionic intermediates, Z_{5w} , by a stronger donor Y'=O than Y'=S. A stronger negative charge on Y will result in a larger solvation stabilization by a stronger hydrogen bond formation. The increase in the negative charge on the Y atom from Z_{0w} to Z_{5w} [$-\Delta q(Y) = q_Y(Z_{5w}) - q_Y(Z_{0w})$] was larger for Y'=O than Y'=S: (O, O; 0.074) vs. (O, S; 0.068), and (S, O; 0.139) vs. (S, S; 0.129). The solvation stabilization of Z_{5w} zwitterions, ΔE_s , is influenced more strongly by the strength of negative charge on Y, q_Y , than by that on the positive charge on NH₃ group, q_{NH_3} , since the negative charge on Y is much stronger, e.g., for (O, S) $q_Y = -0.6139$ but $q_{NH_3} = +0.3624$. This is also supported by the magnitude of solvent assistance, ΔE_{sa} in table 3, calculated at the B3LYP/6-311 + G**//B3LYP/6-31G** level, which decreases in the order, (O, O: $q_Y = -0.678$; $q_{NH_3} = +0.355$) > (O, S: -0.626; +0.362) > (S, O: -0.465; +0.437) > (S, S: 0.457; +0.452). It should be noted that the magnitude of the negative charge on Y, q_Y , decreases, whereas that of positive charge on the NH₃ group, q_{NH_3} , increases, with a decrease in the magnitude of ΔE_{sa} value. The solvent assistance can be considered as the ionic solvation energy of zwitterions, since the bare (five explicit water molecules are deleted and at unrelaxed state) zwitterions are solvated by five water molecules in the process, (see figure 1). The average solvent assistance energy per water, $\Delta E_{sa}/5$ in table 3, is ca -54.4–58.6 kJ/mol, which is in the range of the average experimental hydration energy of a chloride ion, Cl⁻, in water, -54.4 kJ/mol for $n < 5$ [27]. The result of this comparison suggests that the solvent assistance energy is really the hydration energy of the negative Y⁻ ion in Z_{5w} by five water molecules.

3.2 Carbamates

The general pattern of the structures of penta-hydrated zwitterionic complexes are again similar irrespective of the variation of Y, Y' as shown for the thiono carbamate in figure 3.

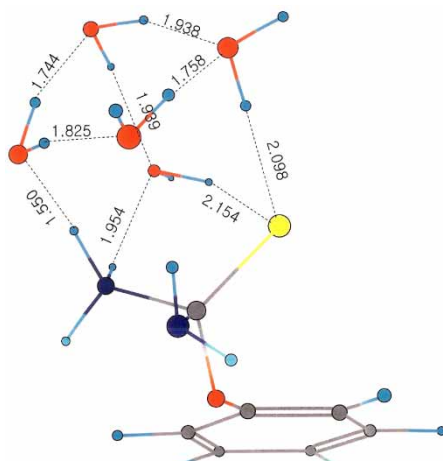


Figure 3. The B3LYP/6-31G** Z_{5w} structure for carbamate (S, O), (benzene ring is shown partly). Bond lengths are in Å.

The trends of changes with a variation of atom pairs Y, Y' (O or S) in the reorganization (ΔE_{re}) and solvation energies (ΔE_s), and solvent assistance (ΔE_{sa}) for zwitterionic intermediates, Z_{5w} , in the carbamate aminolysis are similar to those for the aminolysis of carbonates, discussed above, table 6. We note, however, that the magnitude of MP2 ΔE_s values are considerably larger than those by other methods. This could be due to overestimation of electron correlation energy effects by the MP2 theory for the relatively strong charge transfer delocalization [28–30] involved in the H-bonding networks within the Z_{5w} structures. On the other hand, the magnitude of the ΔE_{re} values are distinctly the largest, whereas that of the ΔE_s values are the smallest, for the carbamates among the three series studied so far, *i.e.*, esters, carbonates and carbamates **1–3**. This means that the formation of intermediates Z_{5w} is the most difficult, and the stabilization of Z_{5w} by five water molecules is the least in the carbamate aminolysis. Meanwhile, the magnitude of ΔE_{sa} is quite similar for the three series, which is reasonable since the overall energies acquired from the H-bonding of five water

Table 6. Comparison of ΔE_{re} , ΔE_s and ΔE_{sa} for Z_{5w} of esters, carbonates and carbamates at the B3LYP/6-311 + G**//B3LYP/6-31G** level (kJ/mol).

Y, Y'	O, O	O, S	S, O	S, S
		ΔE_{re}		
esters	150.5	133.9	122.5	108.9
carbonates	166.4	173.4	148.9	164.1
carbamates	178.7 (164.5) ^a	185.7 178.2	163.8 138.3	171.9 150.4
		ΔE_s		
esters	-143.8	-156.1	-167.5	-174.8
carbonates	-132.2	-113.6	-132.3	-116.3
carbamates	-116.7 (-234.5) ^a	-107.1 (-226.6)	-124.8 (-234.7)	-109.9 (-226.3)
		ΔE_{sa}		
esters	-294.2	-290.0	-290.0	-283.7
carbonates	-298.6	-287.1	-281.2	-280.5
carbamates	-295.3 (-399.0) ^a	-292.8 (-519.4)	-288.6 (-523.3)	-281.8 (-508.1)

^aMP2/6-31G** values.

molecules forming nine H-bonds should be similar, irrespective of the different non-leaving group (R, RO or RNH in **1–3**) within zwitterions Z_{5w} . In other words, the formation and stabilization of the putative zwitterionic tetrahedral intermediates are the most favorable in the ester aminolysis, but are the most unfavorable in the carbamate aminolysis, with the carbonate aminolysis being in between. This strongly unfavorable zwitterion formation and low stability in the carbamate aminolysis could be the reason for the experimentally observed mechanistic changeover to a concerted process for the carbamate, *i.e.*, the zwitterions, Z_{5w} , are either cannot exist (unforced concerted) or they are so unstable that the concerted process offers lower energy pathway for the carbamates [16]. For the concerted aminolysis of carbamates, experimental rate order is exactly a reverse of the sequence for esters [16], rate order (1). In this case, the rate order follows the electrophilicity (or the strength of positive charge) of the carbonyl carbon in the carbamates. Our NBO analysis in table 6 shows that the low stability of the carbamates can be attributed to the strong vicinal charge transfer from a non-bonding orbital of the NH_2 nitrogen (n_N) to the vacant $\pi_{C=Y}^*$ orbital, $n_N \rightarrow \pi_{C=Y}^*$ interaction. As a result of this interaction, the bond length of $\pi_{C=Y}$ bond elongates and the overlap (and hence the Fock matrix element, $F_{n\pi^*}$) between the two interacting orbitals, $n_{Y'}$ and $\pi_{C=Y}^*$, decreases so that the ΔE_{re} value is raised ($\Delta S_{n\pi^*} < 0 \rightarrow \Delta F_{n\pi^*} < 0 \rightarrow \Delta SE < 0 \rightarrow \Delta \Delta E_{re} > 0$ in equation 3), substantially. The NBO analysis shown in table 6 clearly demonstrates that due to the greater lone pair donor ability of N than O [25, 26] the SE values by $n_N \rightarrow \pi_{C=Y}^*$ is greater and as a result the SE values by $n_{Y'} \rightarrow \pi_{C=Y}^*$ interactions become smaller for the carbamates than those for the carbonates. The increase in the ΔE_{re} value will lead to a decrease in the ΔE_s value within a given total H-bond energy supplied by five water molecules, ΔE_{sa} value, which is nearly independent of the non-leaving group, R, RO and RNH in **1–3**. We therefore, conclude that the non-leaving group in **1–3** influences the aminolysis mechanism of **1–3** not through changes in the leaving ability, k_b , but through changes in the stability of T^\pm , *i.e.*, equilibrium constant K in the overall rate constant $k_2 = Kk_b$, equation 4.

We can summarize the results of our studies on the stabilities of the zwitterionic intermediates, Z_{5w} , in the aminolysis of esters, carbonates and carbamates, **1–3**, as follows: (i) The relative proclivity to form, and the stability of, a zwitterionic tetrahedral intermediate can be provided by the relative magnitude of the reorganization energy, ΔE_{re} , for Z_{5w} . (ii) The orders of decreasing ΔE_{re} values are in good agreement with the experimental aminolysis rate orders for esters and carbonates as Y, Y' (O or S) are varied, rate orders (1) and (2), respectively. (iii) The relative ΔE_{re} values are largely determined by the relative magnitude of the stabilization energy, SE, due to the vicinal charge transfer from a $p\pi$ type non-bonding orbital on the Y' atom to the vacant $\pi_{C=Y}^*$ orbital, $n_{Y'} \rightarrow \pi_{C=Y}^*$ interaction within the esters, carbonates and carbamates, **1–3**. (iv) The pattern of variation in the ΔSE values of zwitterionic intermediates (Z_{5w}) is in turn set by that of $\Delta \delta \varepsilon_{n\pi^*}$ and of $\Delta F_{n\pi^*}$ for the aminolysis of esters and carbonates, respectively. (v) The ΔE_{re} values are the largest and the solvation stabilizations, $-\Delta E_s$, are the least for the Z_{5w} in the aminolysis of carbamates among **1–3**, which suggests that the intermediates are either cannot exist or so unstable that the concerted process offers the lower energy pathway for the carbamate aminolysis as experimentally observed. (vi) The non-leaving groups, R, RO, and RNH in **1–3** influence the overall aminolysis rate, $\Delta k_2 = \Delta(Kk_b)$, through the change in the stability of the zwitterionic intermediates, ΔK , but not through a change in the leaving ability, Δk_b . This is attributed to the relative strength of vicinal charge transfer interaction of a nonbonding orbital of the methoxy O (CH_3O) and amino N (NH_2) in the carbonates and in the carbamates, respectively, with the $\pi_{C=Y}^*$ orbital. The stronger the interaction, the weaker becomes the SE (weakening in the SE is greater due to $n_N \rightarrow \pi_{C=Y}^*$ than due to $n_O \rightarrow \pi_{C=Y}^*$) as a consequence of a decrease in the overlap (*i.e.*, $\Delta F_{n\pi^*} < 0$) between $n_{Y'}$ and $\pi_{C=Y}^*$.

4. Supporting information

Coordinates and electronic energies of all the optimized Z_{0w} and Z_{5w} structures. This material can be accessed using the web-based edition of the *Journal* only.

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