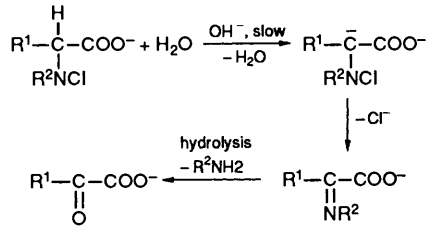
Decomposition of *N*-Chloro-α-amino Acids in Alkaline Medium

X. L. Armesto, M. Canle, M. Losada and J. A. Santaballa *
Universidad de la Coruña, Facultad de Ciencias, Departamento de Química Fundamental e Industrial, A Zapateira, s/n 15071 La Coruña, Spain

The decomposition of the *N*-Cl and *N*-Br derivatives of L-glycine and L-sarcosine in alkaline medium shows a first-order dependence, with respect to the *N*-halo-α-amino acid and to the concentration of hydroxide ions. From the leaving group effect and the primary deuterium kinetic isotope effect, and in the framework of the principle of non-perfect synchronization, the conclusion can be drawn that the decomposition of the *N*-halo-α-amino acids in alkaline medium can be satisfactorily described through an ($A_{xh}D_HD_N$) mechanism with a carbanion and reactant-like transition state.

There is some literature available on the decomposition of *N*-Cl-α-amino acids in conditions close to those of natural waters. In all cases unimolecular decomposition kinetics were observed.[1] Nevertheless, little research dealing with the behaviour of *N*-halo-α-amino acids in alkaline media has been carried out. The first approach to the problem is due to Friedman and Morgulis,[2] who put forward as a slow step the formation of a carbanion which yields an imine that is subsequently hydrolysed to the corresponding α-ketoacid and ammonia (see Scheme 1). Later, Fox and Bullock[3] put forward the same mechanism.



Scheme 1

This supposition agrees with the work of Ingols *et al.*,[4] who found pyruvic acid as a decomposition product of *N*-Cl-alanine at pH *ca.* 8. Stambro and Smith,[5] studying the same system, found a slight increment of the rate constant for pH values close to 7.5, which they justify by means of a second reaction path for the decomposition (in addition to that put forward for lower pH values) *via* the formation of the carbanion. Antelo *et al.*[6] observed for the decomposition of *N*-Cl-serine a noteworthy increase in the rate constant at pH > 9. The results were interpreted on the basis that two reaction paths act simultaneously in these pH conditions in accordance with the proposal of Friedman and Morgulis.[2] The study carried out with *N*-Br-serine[7] showed a similar behaviour, the rate constant increase at pH > 11, with β-hydroxypyruvic acid as reaction product in high yield, which led to the proposal of the same mechanism as that for *N*-Cl-serine. In a previous paper[8] we found an analogous behaviour pattern for the decomposition of *N*-Cl-threonine.

In this paper we analyse the decomposition of the *N*-Cl and *N*-Br derivatives of glycine and sarcosine in alkaline medium.

Experimental

Reagents.—With the exception of [$^2H_5$]glycine, which was Aldrich p.s., all the reagents used were Merck p.a. The sodium hypochlorite solutions were prepared and titrated following the procedure described in a previous paper.[8] The sodium hypobromite solutions were obtained by dissolving bromine in concentrated sodium hydroxide, and titrated spectrophotometrically at pH *ca.* 12, $\lambda_{max}(H_2O)$/nm *ca.* 330 (ε/dm^3 mol^{-1} cm^{-1} *ca.* 324).

The ionic strength (0.5 mol dm^{-3}) was controlled with sodium chloride or sodium perchlorate. All the water used was obtained from a Millipore-Milli Q water purification system.

Table 1 Maxima of UV absorption of the *N*-haloamino acids

N-X-Amino acid	λ/nm
N-Cl-Gly	254
N-Cl-Sar	267
[$^2H_4$]*N*-Cl-Gly	254
N-Br-Gly	288
N-Br-Sar	268
[$^2H_4$]*N*-Br-Gly	288

Procedure.—The *N*-Cl and *N*-Br amino acid (10^{-4} mol dm^{-3}–10^{-3} mol dm^{-3}) solutions were obtained by mixing equal volumes of amino acid and of aqueous hypochlorite or hypobromite solutions at pH 9 and 11 respectively. In all cases an excess of amino acid of more than 40% was used to limit the formation of the corresponding *N*,*N*-dihalo-α-amino acid. Immediately after, appropriate quantities of the NaOH solution were added.

The kinetics of decomposition were studied by following the disappearance of the maximum of UV absorption of the *N*-haloamino acids (see Table 1). The measurements were taken on a UV–VIS (Beckman DU-70) spectrophotometer. The temperature was maintained within ±0.1 K with a Frigiterm 6000382 thermostat. In order to estimate the first-order rate constants, the non-linear monodimensional optimization algorithm due to Davies, Swann and Campey[9] was used. The data were reproducible within 5%.

Reaction Products.—The yield of ammonia was determined with an ammonia NH_3 (152303000) Ingold selective electrode, obtaining 86 ± 10% for the *N*-Cl-glycine. As *N*-Cl-sarcosine yields methylamine, ammonia was not detected in this case.

The glyoxylic acid analysis was carried out by generating its 2,4-dinitrophenylhydrazone as described in the literature.[7] For the *N*-Cl-glycine and the *N*-Cl-sarcosine 100% of α-ketoacid was obtained. The absence of 'active chlorine' at the end of the process was verified by treating an aliquot of the reaction mixture with a solution of potassium iodide buffered with acetic acid/acetate.

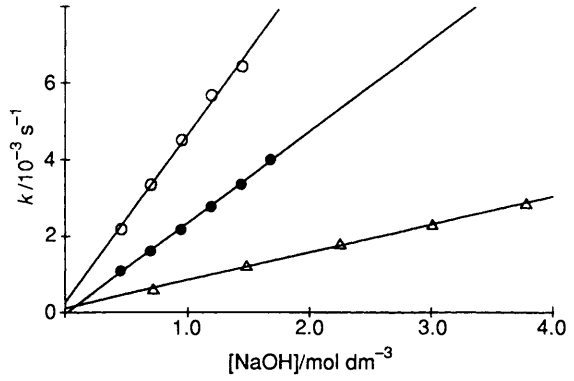


Fig. 1 Influence of [NaOH] on *N*-Cl-amino acid decomposition. ○, *N*-Cl-Gly; ●, *N*-Cl-Sar; △, [$^2H_4$]*N*-Cl-Gly. [Amino acid]/10^{-3} mol dm^{-3} = ○, 3.0; ●, 3.6; △, 3.7. [ClO^-]/10^{-3} mol dm^{-3} = ○, 1.4; ●, 1.4; △, 2.5. *I*/mol dm^{-3} = 0.5 (NaCl). *T* = 298 K.

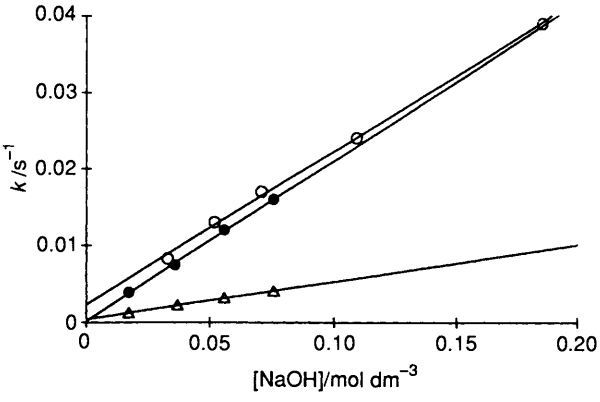


Fig. 2 The influence of [NaOH] on the decomposition of *N*-Br-amino acids. ○, *N*-Br-Gly; ●, *N*-Br-Sar; △, [$^2H_4$]*N*-Br-Gly. [Amino acid]/10^{-3} mol dm^{-3} = ○, 5.3; ●, 3.8; △, 2.8. [BrO^-]/10^{-3} mol dm^{-3} = ○, 2.1; ●, 1.6; △, 1.6. *I*/mol dm^{-3} = 0.5 ($NaClO_4$). *T* = 298 K.

Table 2 k_{OH^-} values for the *N*-haloamino acids

N-X-Amino acid 1	$k_{OH^-}/10^{-2}$ [a]	*N*-X-Amino acid 2	Quotient [b]
N-Br-Gly	19.5 ± 0.3	*N*-Cl-Gly	4.4
		[$^2H_4$]*N*-Br-Gly	4.1
		N-Br-Sar	0.9
N-Br-Sar	20.54 ± 0.3	*N*-Cl-Sar	8.6
[$^2H_4$]*N*-Br-Gly	4.81 ± 0.05	[$^2H_4$]*N*-Cl-Gly	6.6
N-Cl-Gly	4.4 ± 0.2	*N*-Cl-Sar	1.8
		[$^2H_4$]*N*-Cl-Gly	6.0
N-Cl-Sar	2.38 ± 0.04		
[$^2H_4$]*N*-Cl-Gly	0.73 ± 0.07		

[a] Mol^{-1} dm^3 s^{-1}. [b] k_{OH^-}(*N*-X-Amino acid 1)/k_{OH^-}(*N*-X-Amino acid 2).

Results

The analysis of the kinetic data allow us to establish that the process is of first order with respect to the concentration of *N*-haloamino acids (*N*-X-Aa). From the dependence of the observed first-order rate constant k_{obs} on the sodium hydroxide concentration, shown in Figs. 1 and 2, it can be established that eqn. (1) holds, where r_0 represents the contribution due to the unimolecular decomposition process and r_{OH^-} is the contribution due to the base-catalysed process in alkaline medium.

$$r = r_0 + r_{OH^-} = k_0\,[N\text{-Cl-Aa}] + k_{OH^-}\,[OH^-]\,[N\text{-Cl-Aa}] \quad (1)$$

The results obtained for k_0 are within the high experimental error which affects the ordinates in accordance with the published values.[1]

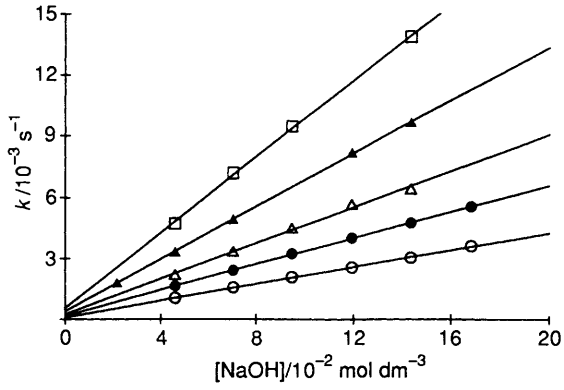


Fig. 3 Influence of [NaOH] on *N*-Cl-glycine decomposition. [Amino acid]/10^{-3} mol dm^{-3} = 3.0, [ClO^-]/10^{-3} mol dm^{-3} = 1.4, *I*/mol dm^{-3} = 0.5 (NaCl). □, 307.0 K; ▲, 302.3 K; △, 298.0 K; ●, 293.6 K; ○, 288.6 K.

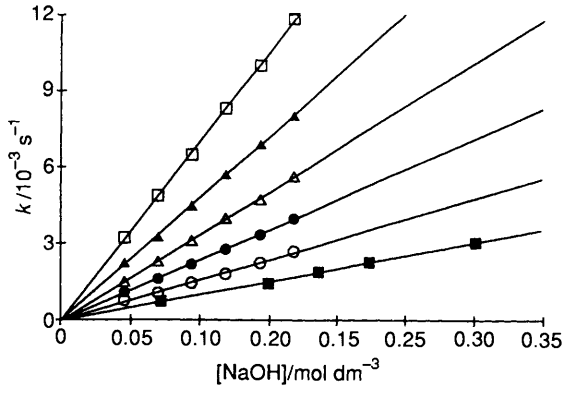


Fig. 4 Influence of [NaOH] on *N*-Cl-sarcosine decomposition. [Amino acid]/10^{-3} mol dm^{-3} = 3.6, [ClO^-]/10^{-3} mol dm^{-3} = 1.4, *I*/mol dm^{-3} = 0.5 (NaCl). □, 310.5 K; ▲, 306.3 K; △, 302.4 K; ●, 298.0 K; ○, 293.0 K; ■, 289.4 K.

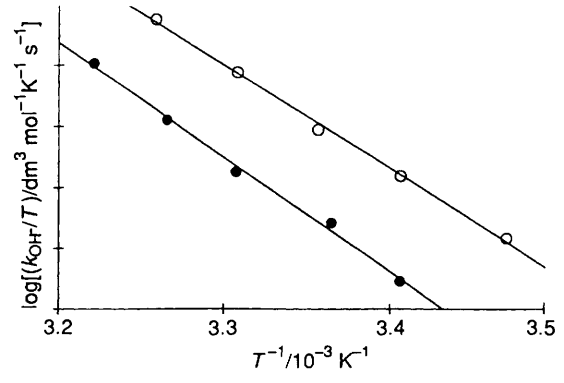


Fig. 5 Plot of $\ln(k_{OH}/T)$ *versus* the reciprocal of absolute temperature. ○, *N*-Cl-Gly; ●, *N*-Cl-Sar.

Table 2 shows the values of k_{OH^-} obtained from the second term of eqn. (1).

The study of the effect of the temperature on the rate constant for *N*-Cl-glycine and *N*-Cl-sarcosine is shown in Figs. 3 and 4. Table 3 collects the values of k_{OH^-} obtained at different temperatures as well as the activation parameters (Fig. 5).

The rate constant also depends on the ionic strength of the medium (Table 4).

The results obtained on studying the isotope effects and the leaving group effects are shown in Table 2.

Table 3 k_{OH^-} temperature dependence and activation parameters[a]

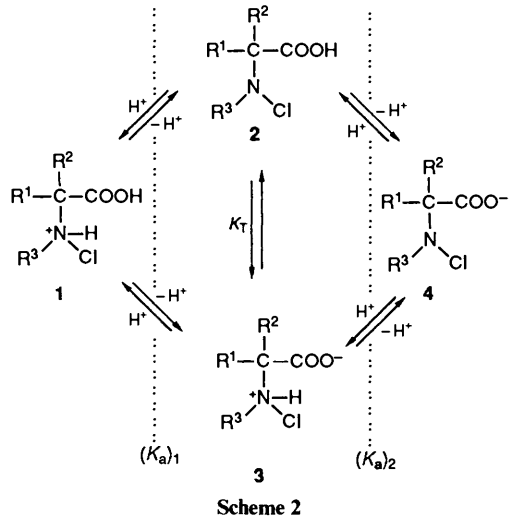
Substrate	T/K	$k_{OH^-}/10^{-2}$ dm^3 mol^{-1} s^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} k^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}
N-Cl-Gly	288.6	2.08 ± 0.04	−83 ± 4	56 ± 2
	293.6	3.21 ± 0.03		
	298.0	4.4 ± 0.2		
	302.3	6.48 ± 0.05		
	306.9	9.4 ± 0.2		
N-Cl-Sar	289.4	1.02 ± 0.01	−64 ± 2	60 ± 3
	293.6	1.60 ± 0.05		
	298.0	2.38 ± 0.04		
	302.4	3.39 ± 0.04		
	306.3	4.81 ± 0.07		
	310.5	7.06 ± 0.08		

[a] [Gly] = 3.0 × 10^{-3} mol dm^{-3}; [Sar] = 3.6 × 10^{-3} mol dm^{-3}; [ClO−] = 1.4 × 10^{-3} mol dm^{-3}; I = 0.5 mol dm^{-3} (NaCl).

Table 4 k_{obs} Dependence on ionic strength[a]

N-Cl-Gly		*N*-Cl-Sar	
[NaCl]/mol dm^{-3}	$k_{ob}/10^{-3}$ s^{-1}	[NaCl]/mol dm^{-3}	$k_{ob}/10^{-3}$ s^{-1}
0.0	3.7	0.0	1.9
0.2	4.3	0.5	2.8
0.4	4.7	1.0	3.6
0.6	4.9	1.5	4.1
0.8	5.0	1.8	4.5
1.0	5.4	2.2	4.9

[a] [Gly] = 3.0 × 10^{-3} mol dm^{-3}; [Sar] = 3.6 × 10^{-3} mol dm^{-3}; [ClO$^-$] = 1.4 × 10^{-3} mol dm^{-3}; [NaOH] = 0.13 mol dm^{-3}; T = 298 K.



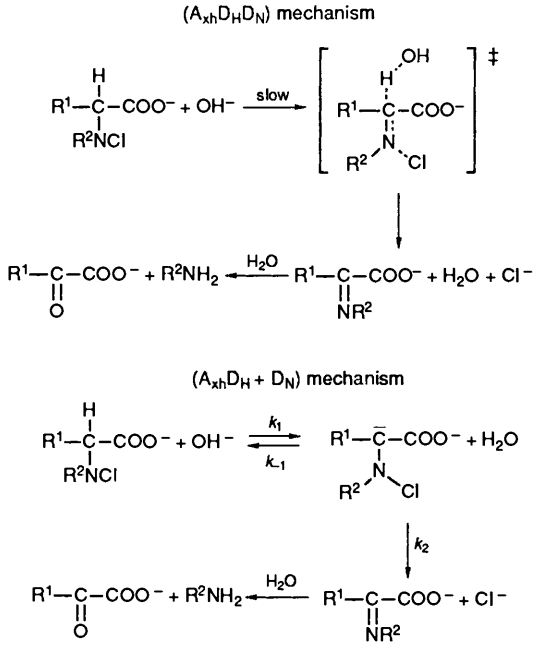
Scheme 2

Discussion

The *N*-X-amino acids may be found in any of the forms which are shown in Scheme 2.

Taking into account the macroscopic pK_a values for glycine[10] (pK_1 *ca.* 2.34, pK_2 *ca.* 9.60) and sarcosine[10] (pK_1 *ca.* 2.23, pK_2 *ca.* 10.02), it can be concluded that the only species present in appreciable concentration would be **3** and **4**. The acidifying effect of the halogen bonded to the nitrogen[11] results in a significant decrease of pK_2, which implies that the *N*-haloamino acids are found exclusively in the anionic form (species **4**).

The reaction must take place through a proton abstraction by the hydroxide ion. This proton could be the one bonded to the nitrogen or the one bonded to C_α.* Despite the presumable higher acidity of the former, the observed behaviour of *N*-halosarcosine indicates that the process involves the participation of the hydrogen on C_α. This is reinforced by the fact that *N*-Cl-derivatives completely substituted at C_α, such as 2-*N*-Cl-aminoisobutyric acid do not exhibit a dependence of the rate constant on NaOH concentration.[12]



Scheme 3

The possible mechanistic alternatives are shown in Scheme 3.

Considering the non-concerted ($A_{xh}D_H + D_N$) mechanism, different possibilities arise depending on the relative values for the rate constants k_1, k_{-1} and k_2. Applying the steady state condition to the carbanion gives eqn. (2)

$$r_{OH^-} = \frac{K_w k_2 k_1 [OH^-][\text{N-Cl-Aa}]}{(k_2 + k_1)(K_w + K_a[OH^-])} \quad (2)$$

Given that ($K_w + K_a[OH^-]$) ≃ K_w, which is to be expected if it is taken into consideration that for compounds like acetone[13] pK_a ≃ 19 in water, the expression (2) becomes eqn. (3) which, by comparison with eqn. (1), gives eqn. (4).

$$r_{OH^-} = \frac{k_2 k_1 [OH^-][\text{N-Cl-AA}]}{(k_2 + k_{-1})} \quad (3)$$

$$k_{OH^-} = \frac{k_2 k_1}{(k_2 + k_{-1})} \quad (4)$$

* Note that although the process is a β-elimination the implied C atom is the one in the α position with respect to the $-CO_2^-$ group.

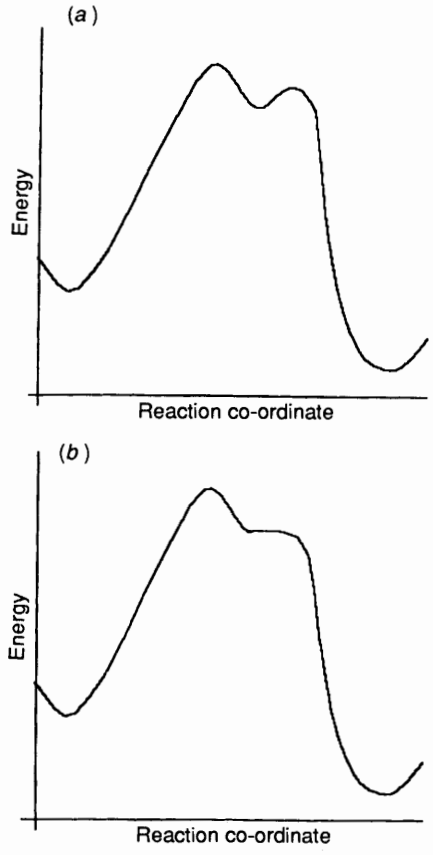


Fig. 6 Reaction co-ordinate diagram. (*a*) A two-step reaction, $A_{xh}D_H^{\ddagger} + D_N$, where the limiting step is the formation of a carbanion. (*b*) Asynchronous two-stage $A_{xh}D_HD_N$ mechanism.

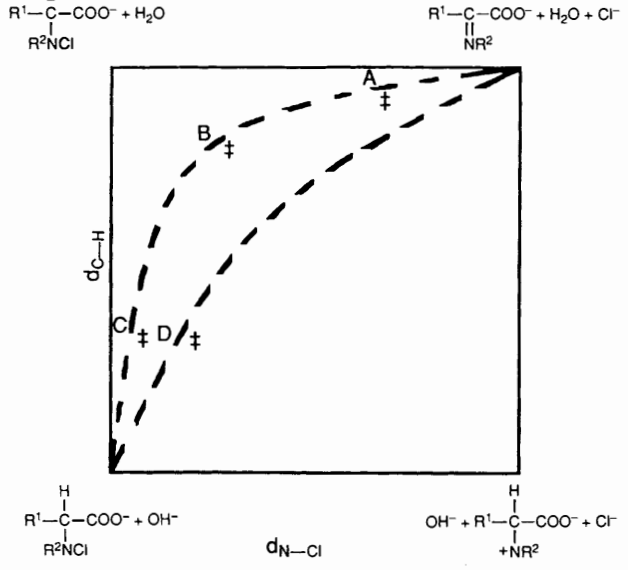


Fig. 7 More O'Ferrall diagram showing alternative positions of the transition state in an $A_{xh}D_HD_N$ carbanion like process

As $k_2 \lll k_{-1}$, this reduces to eqn. (5).

$$k_{OH^-} = \frac{k_2k_1}{k_{-1}} = \frac{k_2K_a}{K_w} \quad (5)$$

Under these conditions the rate-limiting step would be the decomposition of the carbanion formed in the previous equilibrium. This mechanism ($A_{xh}D_H + D_N^{\ddagger}$) is characterized by the absence of isotope effect, contrary to the experimental results. If $k_2 \ggg k_{-1}$, there are two alternative possibilities which are difficult to distinguish: firstly ($A_{xh}D_H^{\ddagger} + D_N$) where the limiting step is the formation of a carbanion as a stable intermediate [Fig. 6(*a*)], $k_{OH^-} = k_1$; and the concerted ($A_{xh}D_HD_N$) mechanism when the elimination of the leaving group is fast with respect to the proton transfer [Fig. 6(*b*)].

The effect of ionic strength and the clearly negative value of the activation entropy, both characteristic of a bimolecular process in which ionic species are involved, agree fully with any of the possibilities described above.

Supposing that the process take place through the ($A_{xh}D_H^{\ddagger} + D_N$) mechanism, the decrease of k_{OH^-} due to the presence of a methyl group (see Table 2) on the nitrogen atom of the *N*-Cl-derivatives, can be attributed to the destabilization of the carbanion caused by the inductive effect of this group.

On the other hand, the effect of the leaving group (Table 2) is minor compared to what was found in $A_{xh}D_HD_N$ processes, such as those undergone[14,15] by CH_3–CH_2–X ($k_{Br}/k_{Cl} = 28$), Ph–CH_2–CH_2–X ($k_{Br}/k_{Cl} = 60$) and[16,17] PhCH(R)N(Cl)CH_3 (R = Me, $k_{Br}/k_{Cl} = 28.8$; R = H, $k_{Br}/k_{Cl} = 11.9$; R = Ph, $k_{Br}/k_{Cl} = 11.1$) but difficult to interpret in the framework of a ($A_{xh}D_H^{\ddagger} + D_N$) mechanism.

The literature refers to the behaviour of systems such as 2-*p*-toluenesulfonyl-1,2-diphenyl-1-haloethane,[18,19] to which an ($A_{xh}D_H^{\ddagger} + D_N$) mechanism is attributed, and which show a leaving group effect similar to that found by us ($k_{Br}/k_{Cl} = 2$). Nevertheless, a stepwise process implies that the reaction intermediate must have a 'real' existence, at least for a time slightly longer than a molecular vibration, without the N–X bond beginning to break. It is therefore difficult to accept that the Br, less electronegative than the Cl, produces carbanion stabilization.

The hypothesis of a ($A_{xh}D_H^{\ddagger} + D_N$) mechanism is complicated by the observation that the leaving group effects for the *N*-X-[$^2H_4$]glycine ($k_{Br}/k_{Cl} = 6.6$) and *N*-X-sarcosine ($k_{Br}/k_{Cl} = 8.6$) are greater than that found for the *N*-X-glycine ($k_{Br}/k_{Cl} = 5.1$).

The value found for the total isotope effect is acceptable for a ($A_{xh}D_H^{\ddagger} + D_N$) mechanism. Nevertheless, it must be taken into account that, in the framework of the Hammond postulate, the proton is more than half transferred in the transition state. The decrease of the isotope effect in the *N*-Br-glycine would imply a more carbanionic transition state (a higher degree of proton transfer), a conclusion not in agreement with the obtained leaving group effect.

The principle of least nuclear motion,[20] and the geminal effect derived from the presence of the two activating groups on C_α, confirm as most probable an ($A_{xh}D_H^{\ddagger} + D_N$) process. On the other hand it must not be forgotten that the $-CO_2^-$ group has a relatively poor carbanion stabilizing capacity[21] and that the cleavage of the N–X bond to form an imine is simpler than that of a C–X bond to form an alkene.

The circumstances described lead us to consider the possibility of a stepwise process through an ($A_{xh}D_H^{\ddagger} + D_N$) mechanism as being not very feasible, a concerted mechanism being more acceptable.

All the experimental results can be interpreted in the framework of an asynchronous $A_{xh}D_HD_N$ mechanism in two phases, of which the second has zero activation energy, *i.e.* a two-stage reaction in the sense defined by Dewar[22] [see Fig. 6(*b*)].

In order to continue our discussion we shall consider the More O'Ferrall diagram[23] (Fig. 7). To interpret the results, we shall resort to a simplication of Thornton's conclusions[24] summarized in three general rules,[25] which refer to the parallel effects according to Hammond, the anti-Hammond for perpendicular effects, and the total effect as a sum of the preceding two.

With reference to the amplitude of the substituent effects, we will consider that the perpendicular or parallel components produced by these substituents will be greater the greater the

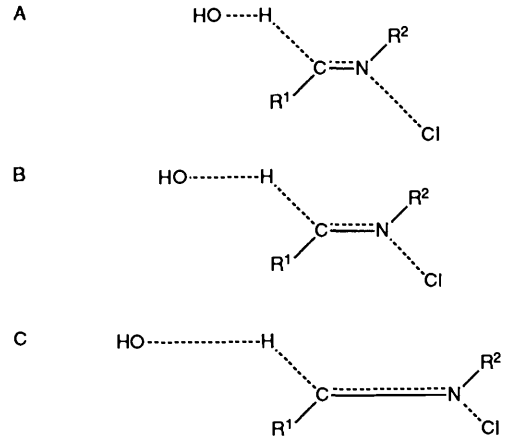


Fig. 8 Possible transition states

bond cleavage which leads to the virtual stabilized species, and that the perpendicular components increase—while the parallels decrease—when the transition state is most displaced in the direction of the component.

On the basis that the process takes place through an $A_{xh}D_HD_N$ carbanion-like mechanism, there are three possible transition states (A, B, C) which are shown on the More O'Ferrall diagram in Fig. 7, and schematically in Fig. 8.

From the energetic point of view the effect on the transition state (Fig. 8) of a *N*-methyl group would gradually change from stabilization in A to a destabilization in C according to the degree of sp^2 hybridisation of the nitrogen and to the degree of cleavage of the N–X bond in the transition state.

The results obtained (Table 2) are in accordance with a transition state similar to C, *i.e.* carbanion and reactant-like. Thus, in *N*-Cl-sarcosine the effect of the methyl group on the transition state with a little developed C=N double bond and a degree of *N*-Cl bond cleavage lower than that of C–H, turns out to be clearly destabilizing.

The substitution of Cl^- by a better leaving group like Br^- would lead to a process closer to the central one, (transition state D, less carbanionic and more nitrenium and reactant-like), which is why the destabilizing effect observed in the *N*-Cl-derivatives is practically undiscernible in the *N*-Br-derivatives, since the stabilizing effect on the virtual nitrenium ion partially compensates for the destabilization of the carbanion.

The methyl group produces two opposite effects: it favours the leaving of the halogen and decreases the proton acidity at C_α. The principle of non-perfect synchronization [26] establishes that of the two effects, the first one to develop *i.e.* the most advanced process in the transition state, will predominate.

In the *N*-Cl-glycine, where we can suppose a transition state with a degree of C–H bond cleavage greater than that of N–Cl, the effect of the introduction of a methyl group on the nitrogen, will be a decrease in the acidity of C_α and, consequently, the destabilization of the process. In *N*-Br-glycine the two effects compensate each other [k_{OH^-} (*N*-Br-Gly) ≈ k_{OH^-} (N-Br-Sar)] which is evidence that the transition state continues to be carbanion-like, given that the methyl effect on the nitrogen, favouring the N–X bond cleavage, is of a similar order, although opposite, to that produced on C_α, one bond further away.

As indicated previously the effect of the leaving group is small for a central $A_{xh}D_HD_N$ mechanism, but not, however, for a ($A_{xh}D_HD_N$) carbanion-like mechanism, where in the transition state the N–X bond cleavage is less than that of the C–H bond.

The high total isotope effect found for *N*-Cl-glycine seems also to be in agreement with the previous suppositions, given that it corresponds to a degree of proton transfer in the transition state close to 50%. A decrease in the carbanionic character is usually accompanied by an increase in the isotope effect,[27,28] provided that, in the transition state, the proton is more than half transferred. The observed decrease in the total isotope effect for *N*-Br-glycine seems to indicate that in the transition state there is less than 50% proton transfer.

Taking into account that the N–X bond has a lower degree of cleavage than the C–H bond, and that the proton of the latter is found closer to C_α than OH^-, it can be concluded that the process can be classified as an ($A_{xh}D_HD_N$) mechanism with a carbanion and reactant-like transition state.

Acknowledgements

The authors would like to thank Professor Rory A. More O'Ferrall for helpful suggestions, and the *Xunta de Galicia* for financial support.

References

1 R. Awad, H. Hussain and P. A. Crooks, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1233 and references therein.
2 A. H. Friedman and S. Morgulis, *J. Am. Chem. Soc.*, 1936, **58**, 909.
3 S. W. Fox and M. W. Bullock, *J. Am. Chem. Soc.*, 1951, **73**, 2754.
4 R. S. Ingols, H. A. Wyckoff, T. W. Kethley, H. W. Hasdgen, E. L. Fincher, J. C. Webrand and J. E. Mandl, *J. Ind. Eng. Chem.*, 1953, **45**, 996.
5 W. D. Stambro and W. D. Smith, *Envir. Sci. Technol.*, 1979, **13**, 446.
6 J. M. Antelo, F. Arce, J. Franco, P. Rodriguez and A. Varela, *Int. J. Chem. Kinet.*, 1988, **20**, 433.
7 J. M. Antelo, F. Arce, J. Crugeiras, J. Franco and A. Varela, *Int. J. Chem. Kinet.*, 1990, **22**, 1271.
8 M. Losada, J. A. Santaballa, X. L. Armesto and J. M. Antelo, *Acta. Chim. Hung. Models in Chemistry*, 1992, **129**, in the press.
9 J. Casado, M. Mosquera, A. Rivas, J. A. Santaballa and M. F. Rodriguez, *Comp. Chem.*, 1983, **7**, 209.
10 *The Merck Index. Centennial Edition*, 11th edn., Merck and Co., Inc., Rahway, N.J., USA, 1989.
11 J. M. Antelo, F. Arce, J. Franco, M. Sanchez and A. Varela, *Bull. Soc. Chim. Belg.*, 1989, **98**, 85.
12 X. L. Armesto, M. Canle, M. Losada and J. A. Santaballa, presented in part at 13° *Encontro anual da Sociedade Portuguesa de Quimica*, Lisboa, January 29–February 2, 1992.
13 Y. Chiang, A. J. Kresge and P. A. Walsh, *J. Am. Chem. Soc.*, 1982, **104**, 6122.
14 E. D. Hughes and V. G. Shapiro, *J. Chem. Soc.*, 1937, 1177.
15 G. H. DePuy and C. A. Bishop, *J. Am. Chem. Soc.*, 1960, **82**, 2535.
16 R. A. Bartsch and B. R. Cho, *J. Am. Chem. Soc.*, 1979, **101**, 3587.
17 R. A. Bartsch and B. R. Cho, *J. Am. Chem. Soc.*, 1989, **111**, 2252.
18 V. Fiandanese, C. V. Maffeo, F. Naso and L. Ronzini, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1303.
19 R. P. Redman, P. J. Thomas and C. J. M. Stirling, *J. Chem. Soc., Chem. Commun.*, 1978, 43.
20 J. Hine, *J. Org. Chem.*, 1966, **31**, 1236; *Adv. Phys. Org. Chem.*, 1977, **15**, 1.
21 J. Crosby and C. J. M. Stirling, *J. Am. Chem. Soc.*, 1968, **90**, 6869; *J. Chem. Soc. B*, 1970, 671; *J. Chem. Soc. B*, 1970, 679.
22 M. J. S. Dewar, *J. Am. Chem. Soc.*, 1984, **106**, 209.
23 R. A. More O'Ferrall, *J. Chem. Soc. B*, 1970, 274.
24 E. R. Thornton, *J. Am. Chem. Soc.*, 1967, **89**, 2915.
25 J. M. Harris, S. G. Shafer, J. R. Moffat and A. M. Becker, *J. Am. Chem. Soc.*, 1979, **101**, 3295.
26 C. F. Bernasconi, *Tetrahedron*, 1985, **41**, 3219.
27 W. H. Saunders and D. N. Edinson, *J. Am. Chem. Soc.*, 1960, **82**, 138.
28 J. A. Marshall and N. Fauble, *J. Am. Chem. Soc.*, 1970, **92**, 948.

Paper 2/04728D
Received 2nd *September* 1992
Accepted 13th *October* 1992