Pergamon

Tetrahedron, Vol. 53, No. 7, pp. 2565-2572, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)01145-3

EVIDENCE FOR AN INTRAMOLECULAR ELIMINATION MECHANISM IN THE AQUEOUS DECOMPOSITION OF (*N*-Cl)-ALCOHOLAMINES

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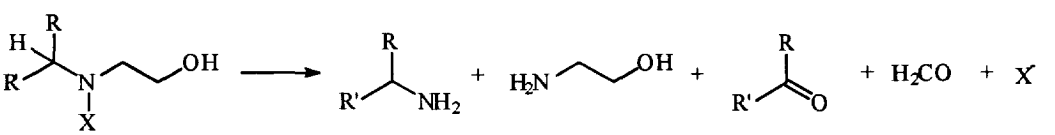
Abstract: (N-Cl)-alcoholamines decompose in aqueous medium through two main reaction paths: an intramolecular elimination and a fragmentation. Both mechanisms take place following a pre-equilibrium deprotonation of the β-hydroxyl group of the (N-Cl)-compound. Evidences for both pathways are given and a very high effective molarity ($EM=0.2\cdot10^6$ M) is reported for the intramolecular process.

Introduction.

The industrial uses of alcoholamines[1] and their subsequent presence in residual waters makes necessary to understand their oxidation processes. Between these, halogenation is still the most employed method of water disinfection. Although different studies are available on this topic,[2,3,4,5,6,7] no explanation has been reported for the abnormal rate enhancements observed in the decomposition of certain (*N*-halo)-alcoholamines, namely (*N*-halo)-ethanolamines (see Scheme 1), relative to (*N*-halo)-amines lacking a β-hydroxyl group.[8] Here, we present a mechanistic explanation for these rate enhancements.

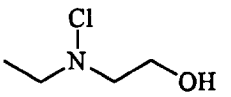
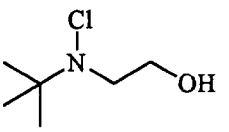
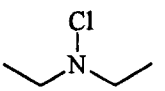


Scheme 1

Experimental.

Aqueous chlorine solutions were used as chlorinating agents and prepared by bubbling Cl_2 (g) through a NaOH solution. The so-obtained solution (NaOCl) was stored in an opaque flask at pH>12 and low temperature, and its concentration spectrophotometrically determined daily (λ_{max}=292 nm, ε=350 $mol^{-1}\cdot dm^3\cdot cm^{-1}$). All other chemicals were Merck or Fluka *p.a.* products. The structure of the employed amines is shown in Table 1.

Table 1: structure of the (*N*-X)-substrates employed.

(*N*-Cl)-Substrate	Structure
(*N*-Cl)-Ethylethanolamine	
(*N*-Cl)-Tertbutylethanolamine	
(*N*-Cl)-Diethylamine	

Bi-distilled water was used to make up the solutions. Repeatedly titrated NaOH solutions were used to generate alkaline medium. The ionic strength was kept to 0.50 mol·dm^{-3} using KCl.

The (*N*-Cl)-amines were generated *in situ* by mixing similar volumes of the chlorinating agent and of the amine solutions, both equally buffered and with the same ionic strength. Once the (*N*-Cl)-amines were generated, NaOH solution was added to promote the decomposition reaction.

The reactions were followed with a single-beam DU-70 Beckman® spectrophotometer and a single-mixing SF-61 Hi-Tech Scientific® stopped-flow spectrophotometer, both thermostatted by water flow to within 0.1 K. The decrease in the absorbance at around 265 nm, characteristic wavelength for the maximum of the (*N*-Cl)-amines, was measured.

The rate constants were obtained by applying the appropriate kinetic equation to the experimental data, using the DSC[9] or Marquardt [10] algorithms.All reported rate constants are average values obtained from replicated experiments, their reproducibility being within 5%.

The product analysis was carried out by spectrophotometric methods. The yields of formaldehyde were quantitatively determined by reaction with acetylacetone.[11] Acetaldehyde was qualitatively detected by reaction with morpholine-sodium nitroprussiate.[12]

Results and discussion.

The decomposition of (*N*-Cl)-alcoholamines follows a first order rate law relative to the concentration of the substrate:

$$r = k_{obs}\cdot[(N\text{-Cl})\text{-alcoholamine}]$$

No effect of the concentration of chlorinating agent or alcoholamine was observed on the rate of decomposition. Conversely, the observed rate constant shows a linear dependence with the concentration of hydroxide:

$$k_{obs} = k_{OH^-}\cdot[OH^-]$$

Table 2 compiles the second order rate constants k_{OH^-} for the studied (*N*-Cl)-alcoholamines, as well as for (*N*-Cl)-diethylamine.[8]

Table 2: second order rate constants (k_{OH^-}) for decomposition of different (*N*-X)-substrates.

(*N*-Cl)-Substrate	k_{OH^-} (observed) / $mol\cdot l^{-1}\cdot dm^3\cdot s^{-1}$	k_{OH^-} ($A_{xh}D_{II}D_N$)[a] / $mol^{-1}\cdot dm^3\cdot s^{-1}$
(*N*-Cl)-Ethylethanolamine	0.82	$9.4\cdot10^{-4}$
	1.21[b]	
(*N*-Cl)-Tertbutylethanolamine	$8.28\cdot10^{-5}$	$4.5\cdot10^{-6}$
(*N*-Cl)-Diethylamine[8]	$2.03\cdot10^{-4}$	---

[a] Values expected for an intermolecular elimination (estimated from a Taft's relationship).

[b] Result obtained in D_2O.

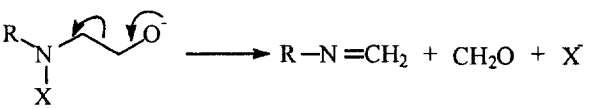
Attention should be drawn to the fact that the catalytic rate constant obtained for (*N*-Cl)-ethylethanolamine is unexpectedly much higher than that of the parent (*N*-Cl)-diethylamine.

Product analysis showed formation of formaldehyde in the decomposition of both studied (*N*-Cl)-alcoholamines, while acetaldehyde was found as an additional product of the decomposition of (*N*-Cl)-ethylethanolamine. Table 3 shows the yields of products:

Table 3: yields of products in the different reactions.

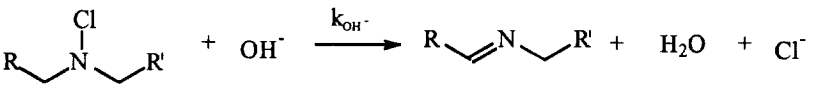
(*N*-Cl)-Substrate	% H_2CO	% CH_3CO
(*N*-Cl)-Ethylethanolamine	27	Detected
(*N*-Cl)-Tertbutylethanolamine	>65	0
(*N*-Cl)-Diethylamine[8]	0	64

The presence of H_2CO as a reaction product is unexpected on the basis of the behaviour observed for (*N*-Cl)-amines lacking a β-hydroxyl group.[8] In order to explain this fact, the fragmentation mechanism shown in Scheme 2 must be considered:[6]



Scheme 2

The presence of acetaldehyde between the reaction products for (*N*-Cl)-ethylethanolamine implies the contribution of $A_{xh}D_HD_N$ elimination process already observed for (*N*-Cl)-amines (shown in Scheme 3).[8,13]



Scheme 3

Table 1 shows the k_{OH^-} values estimated for the N-Cl-alcoholamines from a Taft relationship for N-Cl-amines decomposing exclusively through the $A_{xh}D_HD_N$ mechanism (Scheme 3). Comparison of these values with those experimentally observed show very important differences. The huge increase of k_{OH^-} on going from (*N*-Cl)-diethylamine to (*N*-Cl)-ethylethanolamine allows one to discard the bimolecular $A_{xh}D_HD_N$ elimination as a major reaction pathway, and suggests the existence of a different mechanism.

The fact that the hydroxyl group of (*N*-Cl)-alcoholamines is relatively acidic allows the possibility of an intramolecular elimination (Scheme 4), *i.e.*: an intramolecular abstraction of a H on the C_α to the N would take place following a pre-equilibrium deprotonation of the hydroxyl group of the alcoholamine. A possible way of testing this mechanism is to examine the reaction of a (*N*-Cl)-alcoholamine lacking a H on the the C_α to the N. For this purpose, the decomposition of (*N*-Cl)-terbutylethanolamine in alkaline medium was studied, obtaining a k_{OH^-} value 4 orders of magnitude lower than k_{OH^-} for (*N*-Cl)-ethylethanolamine. This fact is explained on the basis of the impossibility of intramolecular elimination in this case, due to the absence of a H on the C_α to the N. However, the possibility of decomposition of (*N*-Cl)-terbutylethanolamine *via* fragmentation (Scheme 2) or simple bimolecular $A_{xh}D_HD_N$ elimination (Scheme 3) still remains (see Table 2).

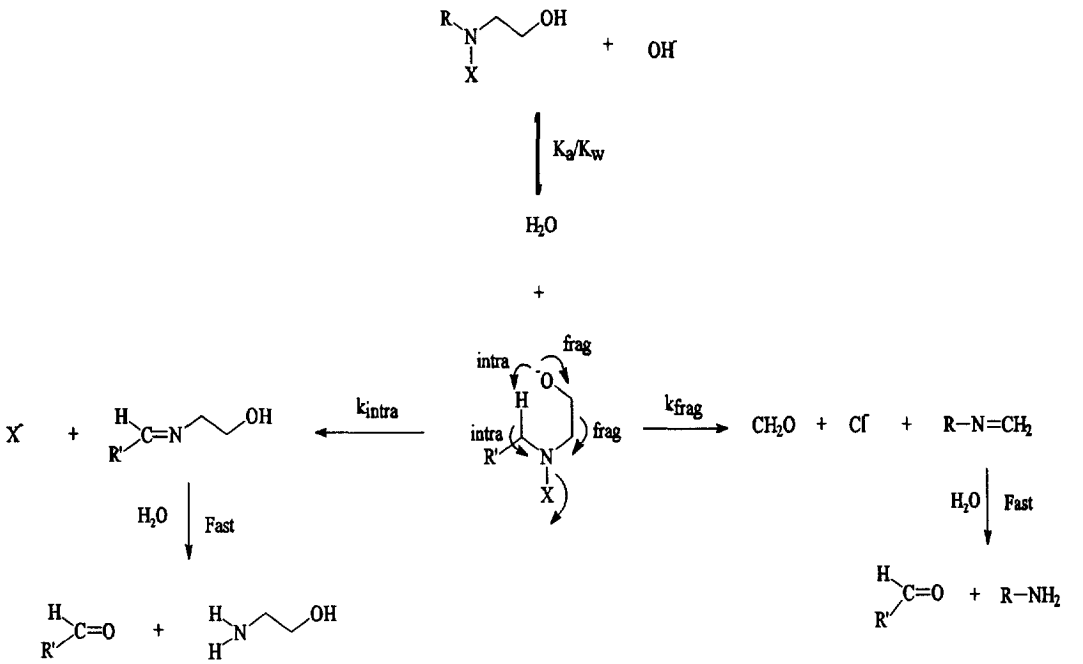
The solvent isotope effect observed in the case of (*N*-Cl)-ethylethanolamine, $(k_{OH^-}/k_{OD^-})_{obs} \approx 0.68$ (Table 2), is characteristic of a pre-equilibrium deprotonation mechanism[14,15] (Table 2), *i.e.*: a fast deprotonation pre-equilibrium:

$$S\text{-}OH + OH^- \rightleftarrows SO^- + H_2O$$

followed by a subsequent slow unimolecular decomposition reaction:

$$S\text{-}O^- \rightarrow [S\text{-}O^-]^{\ddagger} \rightarrow \text{products}$$

The mechanism here proposed for the decomposition of (*N*-Cl)-alcoholamines takes place as shown in Scheme 4. For the sake of simplicity the bimolecular $A_{xh}D_HD_N$ pathway was not included because its contribution is almost negligible.



Scheme 4

Consequently, the rate equation for the decomposition of (*N*-Cl)-ethanolamines is:

$$r = (k_{frag} + k_{intra}) \frac{K_a}{K_w} \cdot [OH^-] \cdot [(N\text{-}Cl)\text{-}Ethanolamine]$$

$$r = k_{uni} \cdot \frac{K_a}{K_w} \cdot [OH^-] \cdot [(N\text{-}Cl)\text{-}Ethanolamine]$$

where K_a and K_w are the ionization constants for (*N*-Cl)-ethanolamines and water, respectively, and k_{uni} is (k_{frag} + k_{intra})

Taking into account the solvent isotope effect for the pre-equilibrium $[(K_a/K_w)_{H_2O} / (K_a/K_w)_{D_2O}] \approx 0.75$,[16] it is possible to estimate the corresponding solvent isotope effect on the rate constant for the unimolecular reaction (k_{uni}):

$$[(k_{uni})_{H_2O} / (k_{uni})_{D_2O}] \approx 0.91$$

This value, close to unity, is consistent with an unimolecular step in which there is no participation of the solvent.

Based on the observed yield of H_2CO and with the values $pK_a \approx 16.5$ (approximate value, based on the

known pK_a's for alcoholamines), $pK_w \simeq 14.0$,[15,17,18] it is possible to estimate the unimolecular rate constants for both the fragmentation (k_{frag}) and the intramolecular (k_{intra}) pathways. These, together with the percentage of reaction that takes place *via* each possible pathway, are summarized in Table 3.

Table 4: different mechanistic pathways and their rate constants.

(*N*-Cl)-Substrate	% Inter	% Intra	% Frag	$k_{frag.}$ / s^{-1}	k_{intra} / s^{-1}
(*N*-Cl)-Ethylethanolamine	<0.1	85-86	13-14	36.4	223
(*N*-Cl)-Tertbutylethanolamine	5-6	---	94-95	0.025	---

From the obtained k_{intra} value and the k_{OH^-} for diethylamine, a minimum effective molarity (EM) can be estimated for the intramolecular elimination pathway:

$$(k_{intra} / k_{inter}) \simeq 0.2 \cdot 10^6 \text{ M}$$

To our knowledge, this is the highest reported EM for this kind of reaction. It is not far from the maximum EM's estimated theoretically by Page and Jencks[19] as 10^8 M and, in a more detailed approach by Mandolini[20] as $10^{6.6}$ M. It is worth remarking that these maximum EM's were estimated for an intramolecular A_ND_N reaction, a process that can be described with only two reaction coordinates, while at least three reaction coordinates are necessary for our $A_{xh}D_HD_N$ process.

Regarding the fragmentation process, although the same pK_a value has been used for both alcoholamines and the k_{frag} values may be affected, the difference is big enough to indicate an important nucleophilic character of the N. This seems to indicate that the driving force of the reaction is the formation of the C=O bond, which is in agreement with similar processes.[21] Moreover, the fact that the obtained k_{frag} is three orders of magnitude higher than the rate constant for the Grob fragmentation of (*N*-Cl)-Sarcosine[20] indicates that H_2CO much better electrofuge than CO_2 in fragmentation reactions.

Further research is in progress in order to improve the knowledge of both the intramolecular and the fragmentation mechanisms.

Conclusion.

The decomposition of (*N*-Cl)-alcoholamines takes places through a two-step mechanism: a pre-equilibrium deprotonation of the -OH group followed by a slow step. When possible, an intramolecular $A_{xh}D_HD_N$ elimination is favoured for this slow step, although a fragmentation reaction takes place as well. The intramolecular reaction shows a very high effective molarity, close to the estimated upper limit for this characteristic parameter.

Acknowledgements.

The authors thank the Xunta de Galicia (project XUGA 10307B95) and the Universidade da Coruña for financial support. We also thank Ms. Eva Couce Carrodeguas for technical help under a grant of the Xunta de Galicia for FP technicians.

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(*Received in UK* 9 *October* 1996; *accepted* 12 *December* 1996)