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THERMAL DECOMPOSITION OF 2-AMINOOXYACID HYDROCHLORIDES AND THEIR ESTERS

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ABSTRACT

Thermogravimetry, differential thermal analysis, and other analytical methods have been applied to the investigation of the thermal behaviour of the compounds of the general formula $RCH(ONH_2.HCl)COOR'$, where R= Me, Et, n-Bu, i-Bu, $PhCH_2$ and R'= H, Me, Et. The decomposition of the compounds is initiated by the rupture of the weakest bond in the molecule, i.e. O - N bond. As a result NH_4Cl and presumably appropriate α-ketoacids or their esters are formed. These compounds undergo volatilization upon heating and this process is accompanied by their further dissociation.

INTRODUCTION

Much attention has been devoted in recent years to the examination of the properties of 2-aminooxyacids and their derivatives. These compounds are interesting from a purely chemical point of view. Moreover, some of them exhibit biological activity [1].

Owing to the presence of an oxygen atom in the molecules of the compounds investigated, their properties differ markedly from those of α-aminoacids. At least some of these properties can be revealed by the knowledge of the behaviour of the compounds upon heating. Present work is devoted to this problem.

MEASURING METHODS

The 2-aminooxyacid hydrochlorides, and appropriate esters were synthesized according to the scheme reported by Testa et al. [2].

The thermal analyses were carried out on an OD-103 derivatograph (Monicon). For the identification of the reaction products, decompositions were performed in the quartz reactor [3] (Fig. 1b) in a continuous flow of the argon stream. The liberated gases were carried off the reaction zone and absorbed in appropriate liquid phases. Organic substances were absorbed in 1,4-dioxane and identified by GLC. Carbon monoxide was detected with $PdCl_2$ solution [4]. The gaseous products was checked for the

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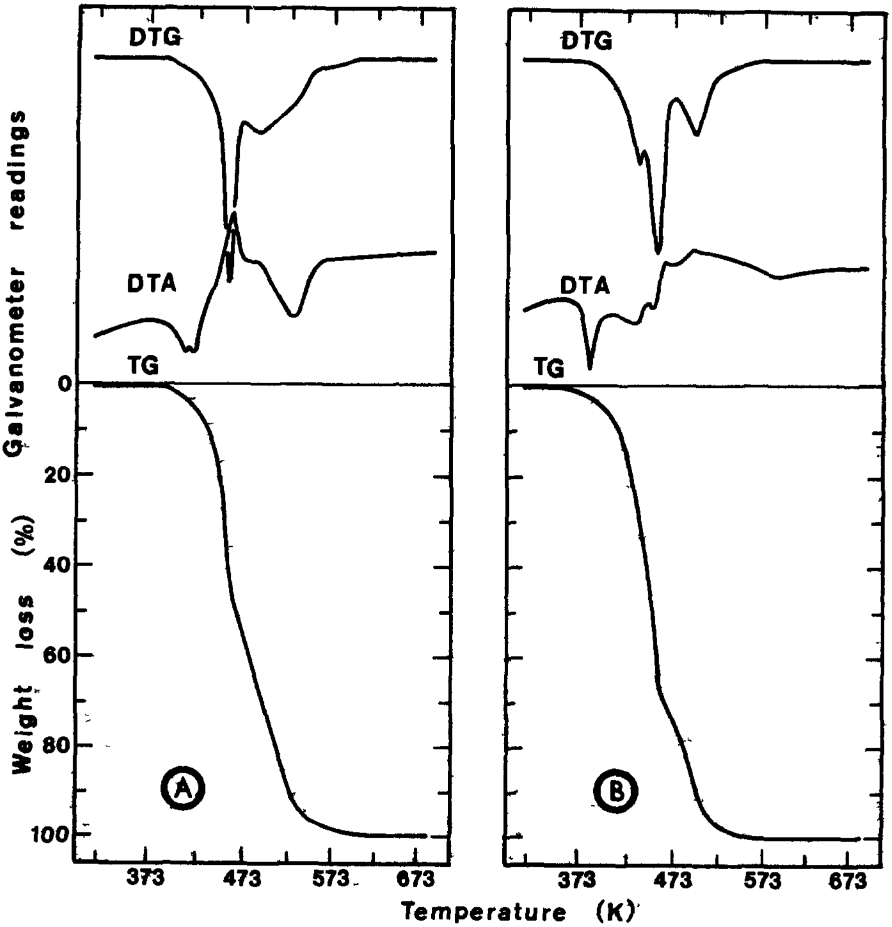

Figure 1. Thermal analyses of 2-aminooxy-4-methylpentanoic acid hydrochloride (A) and its methyl ester (B). Mass of samples = 50 mg; heating rate, 5 K/min; reference material, α-Al_2O_3; sample holder, platinum crucible [5] (Appendix 1, No. 1); galvanometer sensitivities: DTG = 1/10, DTA = 1/3 and TG = 50 mg; dynamic atmosphere of N_2.

presence of CO_2 by absorption in $Ba(OH)_2$ solution. NH_4Cl was identified on the basis of the presence of Cl^- and NH_3.

RESULTS AND DISCUSSION

Thermal analysis curves recorded by a derivatograph for two compounds chosen as examples are shown in Fig. 1. All the compounds studied present multi-step thermal decomposition pattern. The characteristic feature of their thermolysis is that they undergo total volatilization upon heating to 600 K. It can be also noticed that decomposition of the compounds is preceded by melting. The temperatures of the onset of the decomposition are somewhat higher in the case of acids then appropriate esters. The differential thermal analysis curves are characteristic for a given compound investigated and no general regularities in the appearance of DTA peaks are seen. On the other hand, thermogravimetric curves show that dissociation of all the compounds principally proceeds in two stages although in DTG curves of some of them more than two peaks are seen. Examination of TG traces for esters indicates that the compounds lost about 2/3 of their weight in the first step, whereas, during decomposition of acids the mass loss for the first step is equal ca. 1/3 of the mass of the sample. Moreover, in the case of the latter compounds the commencement of the second step is usually associated with the appearance of a fairly strong exothermic effect. It would suggest that oxidation processes occur.

Numerous similarities in the course of the thermal decomposition of the compounds of both groups suggest that the nature of the primary process is the same. Taking into account the values of energies of all the chemical bonds present in molecules, one can conclude that the weakest one is always O - N bond (ca. 80 kJ/mole) [6]. Further considerations regarding various possible pathways for primary decomposition, based on the Hess law and the values of the bond energies [6], revealed that eqn (1) is representing the lowest energy decomposition channel for both acids and esters.

$$RCH(ONH_2.HCl)COOR'_{(s)} \longrightarrow [RCOCOOR']_{(l,g)} + NH_4Cl_{(c)} \qquad (1)$$

As the compounds in square brackets are unstable, they undergo further decomposition which, as it was proved experimentally, leads to their decarbonylation [7,8]. Therefore, we propose reaction (2) as accounting for the mass loss corresponding to the first step of the thermal decomposition of esters of 2-aminooxyacid hydrochlorides.

$$[RCOCOO']_{(l,g)} + NH_4Cl_{(c)} \longrightarrow CO_{(g)} + RCOOR'_{(g)} + NH_4Cl_{(c)} \qquad (2)$$

The esters formed in reaction (2) appear in temperatures above their boiling points. Thus, they undergo instantaneous volatilization. If this is not accomplished, the rate of the release of

CO to the gas phase can exceed somewhat the rate of evaporation of esters. In the latter case additional peaks in DTG curves can appear. The peak temperatures in DTG corresponding to the second step agree satisfactorily with the temperature of volatilization of NH_4Cl [9]. This means that the remaining NH_4Cl is transfered to the gaseous phase in the second stage.

The release only CO to the gas phase can not account for the total mass loss in the first step of the thermal decomposition of 2-aminooxyacid hydrochlorides. On the other hand, the weight loss corresponding to the first step is too low to account for the simultaneous volatilization of both CO and appropriate carboxylic acid. The latter compounds could be formed in the process analogous to that shown by eqn (2). Since the boiling points of these carboxylic acids are higher than those for appropriate esters,therefore, they probably do not undergo the instantaneous volatilization at temperatures corresponding to the first step of the process. As a result, both acids and NH_4Cl undergo volatilization in the second stage which, as one can expect, exhibit a complex nature.

It is worthwhile to mention that the process of the thermal decomposition of α-ketocarboxylic acids can have more complex nature [10]. In the presence of O_2 oxidation processes may occur. Moreover, in higher temperatures dehydration processes can occur which can lead to untypical products.

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