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THERMAL PROPERTIES AND THERMOCHEMISTRY OF HYDROCHLORIDES OF 2-AMINOOXYACIDS AND THEIR ESTERS *

ZYGMUNT WARNKE and JERZY BŁAŻEJOWSKI
Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk (Poland)

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ABSTRACT

Thermal properties of hydrochlorides of some 2-aminooxyacids and their esters of general formula $RCH(ONH_2)COOR' \cdot HCl$, where R=H, Me, Et, *n*-Bu, *i*-Bu, Bz, and R'=H, Me, Et, were examined with thermal analysis methods (DTA, TG, DTG) and by application of standard procedures enabling the identification of reaction products. Heating of the compounds at a constant rate leads to their total volatilization. Thermal decomposition is presumably initiated by the cleavage of the weakest bond in the molecule, i.e. the O–N bond. Secondary processes lead to the formation of carbon monoxide, ammonium chlorides, and organic products whose presence can be explained by assuming the existence of $R^{\cdot}$ and $^{\cdot}COOH(R')$ as intermediates.

To examine the thermodynamics of the thermal decomposition several thermochemical characteristics, such as the enthalpies of formation of gaseous 2-aminooxyacids and their esters, the enthalpies of formation of their crystalline hydrochlorides, the enthalpies of overall and partial processes, and vapour pressures of reaction products at certain decomposition temperatures, were derived using the group additivity methods and available literature data. The thermodynamics of two isomerization processes (i-$Bu^{\cdot} \rightleftharpoons t$-$Bu^{\cdot}$ and 2-$MePh^{\cdot} \rightleftharpoons Bz^{\cdot}$) have been considered also to account for the formation of some of the reaction products. This information was used to elucidate the nature of the thermal decomposition of the compounds studied.

INTRODUCTION

Numerous naturally occurring and synthetic compounds containing the aminooxy group exhibit biological activity. Thus, the antibiotic cycloserine, being a cyclic derivative of 2-amino-3-aminooxypropanoic acid [2], and several 2-aminooxyacids [3,4] and analogues of peptides in which the peptide linkage is replaced by –CONHO– [5], possess a broad range of antibacterial and antifungal activities. Some of these compounds are known as potential growth-inhibitors of many organisms and viruses [6]. Certain 2-aminooxyacids [7–10], and appropriate peptide analogs [11] exhibit neurotropic prop-

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erties, and this topic has recently been thoroughly investigated. Furthermore, aminooxyacetic acid has been shown to increase the production of certain hormones [12]. It is also worth mentioning that some aminooxyacids have been proposed as herbicides [13].

Despite the considerable practical importance of some aminooxyacids their chemical and physical properties have been examined only occasionally. Generally, these compounds exhibit a totally different behaviour compared with that characteristic of aminoacids. This is mostly due to the presence of the O–N bond in molecules of aminooxyacids. Since the O–N bond, similar to the O–O and N–N bonds, is much weaker in comparison with typical chemical bonds [14–17], it might be expected that this would affect significantly the thermal stability and thermal properties of these derivatives. Thus, the study of the thermal behaviour of aminooxyacids is important scientifically and should also provide important information for potential users.

In this work some aspects of the thermochemistry of these compounds are studied.

EXPERIMENTAL

The 2-aminooxyacid hydrochlorides and appropriate esters were synthesized by described methods [18,19].

The thermal analyses were performed on an OD-103 derivatograph (Monicon) with α-Al_2O_3 as reference, in a dynamic atmosphere of nitrogen. The sample was placed in a platinum crucible (ref. 20; Appendix 1, No. 1) and in one experiment (c.f. Fig. 2B) on a platinum plate (ref. 20; Appendix 1, No. 4). Other operating conditions were: mass of sample = 50 mg, heating rate = 5 K min^{-1}, sensitivities of DTG, DTA, and TG galvanometers = 1/10, 1/3, and 50 mg, respectively.

In order to identify the organic products of the thermal decomposition solid samples were introduced directly into an injector of a gas chromatograph heated before analysis to a temperature above the threshold for thermolysis. All analyses were carried out on a Pye Unicam Model 104 gas chromatograph using an SP-1200 phase supplied by Supelco. Carbon monoxide was detected with $PdCl_2$ solution [21]. Amine hydrochlorides were identified by the presence of Cl^- and amines.

RESULTS AND DISCUSSION

1. General features of the thermal decomposition

Thermal analysis curves recorded by a derivatograph for three compounds chosen as examples are shown in Figs. 1 and 2. Table 1 shows

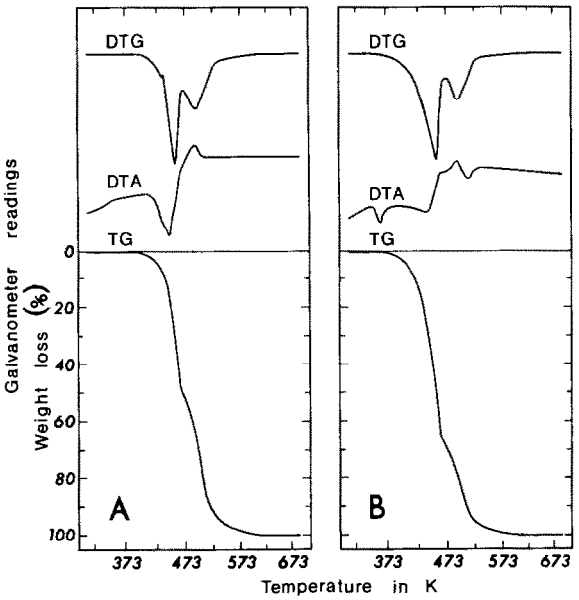


Fig. 1. Thermal analyses of hydrochlorides of 2-aminooxypropanoic acid (A) and its ethyl ester (B).

characteristic parameters resulting from the examination of the thermal analysis curves, along with available information from the literature.

Thermal decomposition of all the compounds studied presents a multi-step

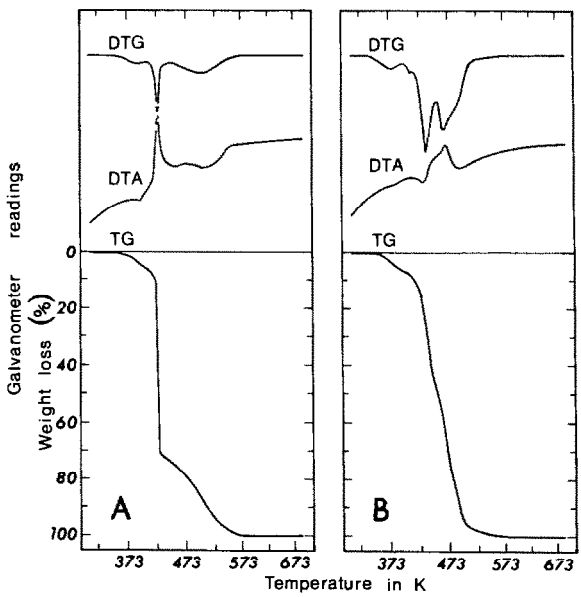


Fig. 2. Thermal analyses of aminooxyacetic acid hydrochloride: platinum crucible (A) and platinum plate (B) as the sample holders, respectively.

TABLE 1

The thermal analysis data for hydrochlorides of 2-aminooxyacids and their esters

Substance [a] $RCH(ONH_2)$-$COOR' \cdot HCl$		Temperature (K) and character of peaks in: [b,c]					Temperature [b] (K)	
		DTG	DTA				$T_{0.01}$	$T_{0.99}$
			Exo-	Endo-				
			T_p	T_m		T_p		
				This work	From literature			
R=H;	R'=H	425s, sh 492m, b	425s, sh	391w	388–389 [d]	506m, b	375	570
R=Me;	R'=H	456s, sh 495s, b	494m	434w	436–437 [d] 436–438 [e]	442s	385	580
R=*n*-Bu;	R'=H	456s, sh 493s, b	464w 493m	395m, sh	385 [d] 383–386 [e]	430w 513w	390	575
R=*i*-Bu;	R'=H	460s, sh 488m, b	463m, sh 484w	407m	445–446 [e] 408–418 [f]	417m 525m	390	575
R=Bz;	R'=H	450s, sh 498m, b 533m, b	461m 492m	409w	448–450 [e]	430w 525m, b 580w	390	595
R=Me;	R'=Et	456s, sh 495m, b	465w 493w	362m, sh	355–356 [g] 358–360 [h]	434m, b 513w	380	565
R=Et;	R'=Me	435w 453s, sh 493m, sh	468w 492w	403m, sh		435w 453w 503w	380	555
R=*i*-Bu;	R'=Me	433w 452s, sh 495m, b	462w 494w	383m, sh		431w 450w	375	540

[a] Me = methyl, Et = ethyl, *n*-Bu = butyl, *i*-Bu = 2-methylpropyl, and Bz = phenylmethyl.
[b] The symbols were taken from ref. 22. T_p = temperature of the peak, T_m = temperature of melting, and T_α = temperature at which the fraction reacted is equal to α (i.e. $T_{0.1} = T_{\alpha=0.1}$).
[c] w = weak, m = medium, s = strong, sh = sharp, and b = broad.
[d] Ref. 6.
[e] Ref. 18.
[f] Ref. 23.
[g] Ref. 19.
[h] Ref. 24.

pattern which is different from that characteristic for 2-amino- [25] or 2-hydroxycarboxylic acids [26]. The thermoanalytical curves are characteristic for each compound examined, although some general regularities in the appearance of the thermal effects is revealed. A characteristic feature of thermolysis of these compounds is that they undergo total volatilization upon heating to 600 K. Decomposition of all the compounds is preceded by

melting. The derived values of temperatures of fusion are comparable to those reported in the literature. The temperatures of the onset of decomposition ($T_{0.01}$) are almost the same for hydrochlorides of both acids and esters. This might suggest that the nature of the primary process is similar for both groups of compounds. On the other hand, fairly low values of $T_{0.01}$ apparently result from the low thermal stability of these derivatives. The temperatures at the end of the process ($T_{0.99}$) are slightly lower for hydrochlorides of esters compared with those for acids. The temperature limits for the thermal decomposition ($T_{0.99} - T_{0.01}$) are similarly regular. Thermogravimetric curves show that the dissociation of all the compounds proceeds principally in two stages, although in DTG curves of some more than two peaks are seen. Examination of TG traces for hydrochlorides of esters indicates that they lose about 2/3 of their weight in the first step, whereas, during decomposition of hydrochlorides of acids the mass loss for the first step is equal to ca. 1/3 of the mass of the sample. Furthermore, the thermal decomposition of all the compounds is always associated with the appearance of a fairly strong exothermic effect. This effect is particularly pronounced in the case of aminooxyacetic acid hydrochloride (Fig. 2).

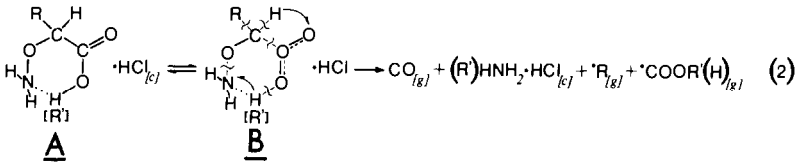
In order to rationalize the nature of the thermal processes an effort was made to identify some of the reaction products. Carbon monoxide and ammonium (or alkanaminium) chlorides were always detected among the reaction products. We could not detect CO_2 using saturated $Ba(OH)_2$ solution. For GC investigations representative compounds have been chosen which promised to provide the most valuable information regarding the decomposition pathways. These were the hydrochlorides of 2-aminooxy-3-phenylpropanoic acid (**I**) and methyl ester of 2-aminooxy-4-methylpentanoic acid (**II**). Thermal decomposition of (**I**) results in the formation of phenylacetic acid and 2-methylbenzoic acid while thermolysis of (**II**) afforded 3-methylbutanoic acid and small amounts of its methyl ester, together with trimethylacetic acid.

2. Nature of the primary process

On the basis of the identified reaction products eqn. (1), which summarizes the overall decomposition process, can be written

$$RCH(ONH_2)COOR' \cdot HCl_{(c)} \rightarrow CO_{(g)} + (R')HNH_3Cl_{(c)} + RCOOR'(H)_{(g \text{ or } c)} \quad (1)$$

It is difficult to predict, with any degree of certainty, the pathways for this process; however some suggestions can be made on the basis of chemical intuition. Building models for various 2-aminooxyacids or their esters it may be seen that characteristic functional groups can be located in such a way as to form a six-membered ring (Scheme I (A)). This structure of 2-amino-



Scheme I. The possible thermal fragmentation pattern of 2-aminooxyacid derivatives.

oxyacids may already exist in the solid phase and could be stabilized by the formation of a strong hydrogen bond or dipolar ion. The latter rearrangement is very likely due to the relatively high proton affinity of the $-ONH_2$ group [27,28]. There also exists experimental [29] and theoretical [28] evidence which supports this hypothesis. The applied method of investigation enables only the vibrational degrees of freedom in the molecules to be excited. Therefore, the most probable primary dissociation pathway would be that which requires the smallest amount of energy. A comparison of the values for the energies of all the bonds present in the molecules [30] shows that the O–N bond is always weakest (ca. 160 kJ mol^{-1} [14,15,30]). The cleavage of the O–N bond in the primary step is even more likely since it is probable that the process does not necessitate overcoming any activation barrier apart from that resulting from the thermodynamical requirements [15]. The scission of the O–N bond has been assumed to be a primary step in the direct [31] and Hg-sensitized [32] photodecomposition of hydroxylamine; some theoretical considerations tend to confirm this concept [33].

Cleavage of the O–N bond causes further changes in the molecule which could resemble those outline in Scheme I (B). The schematic representation of B, proposed as a transition state, is only a heuristic one. Thermal decomposition might well proceed stepwise and may involve an electron, as well as H, or even R′ transfer.

To account for the formation of organic products it is necessary to assume the existence of kinetically free R radicals since only such species are capable of rearrangement to form other structures. This seems to indicate that cleavage of the C–C(R) bond occurs. Subsequent steps might involve the scission of further bonds and may possibly lead to the simultaneous release of CO and to the formation of other intermediate species, such as ·COOH or ·COOR′. Furthermore, the presence of carboxylic acids during decomposition of esters might suggest that R′ transfer takes place. In the latter step the formation of NH_3 or $R'NH_2$ may also be expected. In support of this concept R radicals have been identified by a variety of methods, e.g. Bz· [34–36], or *i*-Bu· [37,38], and their properties are well established [39–42]. On the other hand, the ·COOH and ·COOR′ species have been found in chemical reactions [43], UV and IR photochemical decomposition [44,45], and thermal decomposition [46] of some carboxylic acids derivatives. Moreover, the carboxy radical is formed in the reaction of

CO with ·OH [47] and with water [48]. Some of these radicals have been also identified from γ-radiolysis of aminoacids, e.g. phenylalanine [36].

3. Secondary processes

For all radicals formed several secondary pathways are available. The products observed clearly demonstrate, however, that only cross-combination actually takes place. We could not detect any products which would indicate the participation of dimerization processes. Decomposition of ·COOH (or ·COOR′) to CO_2 and H (or R′) must also be excluded since carbon dioxide has not been detected among the reaction products. Such a process might have been expected as it requires only a small kinetic barrier to be overcome [46,47,49]. All these facts imply that radical processes proceed in the "cage" created by surrounding molecules of substrate and forming ammonium or alkanaminium chlorides. This "cage" is apparently more hermetic than those in the case of liquid phase radical processes since it does not allow the diffusion outside of intermediate species.

The organic products observed upon decomposition of hydrochlorides of 2-aminooxy-3-phenylpropanoic acid and the methyl ester of 2-aminooxy-4-methylpentanoic acid also demonstrate that the thermal reorganization of R radicals must take place before the cross-combination with the carboxy radical occurs. The thermal rearrangement of organic radicals is a fairly well known phenomenon [39,41,42,50–52], with a low activation barrier only and thus can be realized at moderate temperatures [50,52].

To clarify this subject let us examine the thermodynamics of two isomerization processes

$$i\text{-Bu}^{\cdot} \rightleftharpoons t\text{-Bu}^{\cdot} \qquad \Delta G^0_{298} = -20.3 \text{ kJ mol}^{-1} \tag{3}$$

$$2\text{-MePh}^{\cdot} \rightleftharpoons \text{Bz}^{\cdot} \qquad \Delta G^0_{298} = -81.8 \text{ kJ mol}^{-1} \tag{4}$$

where 2-MePh· represents the 2-methylphenyl radical. Since the pertinent ΔG^0 values for these reactions are not available we estimated them on the basis of appropriate ΔH^0 and S^0 values. $\Delta H^0_{f,g}[i\text{-Bu}^{\cdot}]$ was assumed to be 60.7 kJ mol^{-1} [53–55]. There has been a controversy with regard to the correct value of $\Delta H^0_{f,g}[t\text{-Bu}^{\cdot}]$ [41,56]. We assumed this value to be 40.2 kJ mol^{-1} which is a compromise between those reported in the recent literature [41,55–57]. For $\Delta H^0_{f,g}[2\text{-MePh}^{\cdot}]$ we assumed a value equal to 277.5 kJ mol^{-1} which is 19.3 kJ mol^{-1} higher than that calculated by Khrapkovskii et al. [58]. This correction results from the difference between the value of $\Delta H^0_{f,g}[\text{Ph}^{\cdot}]$ reported in the literature (mean of the values reported in refs. 53, 58–64 318.1 kJ mol^{-1}) and that calculated by the authors [58] (298.8 kJ mol^{-1}). For $\Delta H^0_{f,g}[\text{Bz}^{\cdot}]$ we assumed a value of 195.6 kJ mol^{-1} which represents the mean of those listed in the literature [53,62,64,66]. The entropies and heat capacities were taken directly from the work of O'Neal

and Benson [50], or were estimated by the method described there. Using this data we calculated that $\Delta H^0_{298} = -20.5$ and -81.9 kJ mol^{-1}, and $\Delta G^0_{298} = -20.3$ and -81.8 kJ mol^{-1} for reactions (3) and (4), respectively. This estimation of ΔG^0 leads directly to the values of [*t*-Bu$^{\cdot}$]/[*i*-Bu$^{\cdot}$] and [Bz$^{\cdot}$]/[2-MePh$^{\cdot}$] at an equilibrium state. They are equal to ~ 3600 and 2.2×10^{14}, respectively. Temperature has little influence on the values of both ratios.

The driving force for reaction (3) indicates that this rearrangement is thermodynamically favourable. However, the system apparently would not reach equilibrium in our experimental conditions, since the observed ratios of trimethylacetic acid/3-methylbutanoic acid are always much lower than that predicted above. This might result from the existence of an activation barrier for reaction (3) [37] which would cause other radical processes to compete with the isomerization process. The ΔG^0 value for reaction (4) is negative which indicates that 2-methylphenyl radicals should rearrange spontaneously to benzyl radicals and this has been confirmed experimentally [39]. Thus it is not clear why the reverse isomerization takes place in our experimental conditions. Presumably, there are other than thermodynamical reasons responsible for this phenomenon. One possible explanation of this discrepancy might come from the mechanistic considerations. The mechanism of radical processes is not yet well understood [67]. Nevertheless, one can imagine that when a COOH radical interacts with Bz$^{\cdot}$ it finds a certain spin distribution in the molecule of its reaction partner. This distribution is such that it favours positions 7, 2, and 4, respectively [68] in the radical attack. In consequence, at least three pathways for the combination process are disclosed. Each reaction pathway has its own characteristic transition state and activation barrier. The ratio found experimentally [2-MePhCOOH]/[BzCOOH] has a value of approximately 10 and exceeds markedly the ratio of spin densities at positions 2 and 7 (0.23) [68]. Nevertheless, this fact tends to support the mechanism discussed earlier. The same model may also be used in the case of cross-combination of $^{\cdot}$COOH and i-Bu$^{\cdot}$, where the ratio of [*t*-BuCOOH]/[*i*-BuCOOH] found experimentally is almost equal to one.

4. Thermodynamics of the thermal decomposition

More advanced discussion of the thermal behaviour of the compounds studied would be possible after examination of the thermochemistry of the decomposition process. Unfortunately, no thermodynamic data have been recorded either for 2-aminooxyacids or for their derivatives and we therefore estimated some of these characteristics. The standard heats of formation of gaseous 2-aminooxyacids and their esters at 298 K were evaluated on the basis of the Benson group's additivity scheme [69]. For this purpose the

TABLE 2

Enthalpies of formation and thermochemistry of the decomposition process [a]

Substance $RCH(ONH_2)$-COOR'·HCl		$\Delta H^0_{f,g}$	$\Delta H^0_{f,c}$	Thermodynamics of decomposition						
				ΔH^0_r			Vapour pressures [b,c,d]			
				For reaction (1) [b,c]	For reaction (2) [c]	For radical cross-combination process [b,c]	RCOOR'(H)		$(R')HNH_3Cl$	
							$T_{0.01}$	T^I_{DTG}	$T_{0.01}$	T^I_{DTG}
R=H;	R'=H	−404	−671	−133	224	−357	1	1	0.001	0.023
R=Me;	R'=H	−429	−696	−161	176	−337	0.78	1	0.002	0.10
R=*n*-Bu;	R'=H	−492	−759	−142	164	−306	0.040	0.88	0.003	0.10
R=*i*-Bu;	R'=H	−497	−764	−158	160	−317	0.069	1	0.003	0.12
				−163 *		−302 *	0.12 *	1 *		
R=Bz;	R'=H	−316	−583	−260	114	−374	0.0002	0.010	0.003	0.078
				−258 *		−454 *	0.0004 *	0.019 *		
R=Me;	R'=Et	−426	−693	−176	225	−401	1	1	0.002	0.10
				(−162)	(176)	(−337)	(0.78)	(1)	(0.002)	(0.11)
R=Et;	R'=Me	−427	−694	−162	212	−374	1	1	0.002	0.089
				(−152)	(168)	(−320)	(0.22)	(1)	(0.002)	(0.065)
R=*i*-Bu;	R'=Me	−474	−741	−182	208	−390	0.61	1	0.001	0.085
				−178 *		−366 *				
				(−154)	(164)	(−317)	(0.030)	(1)	(0.001)	(0.062)
				(−159 *)		(−302 *)	(0.057 *)	(1 *)		

[a] $\Delta H^0_{f,g} = \Delta H^0_{f,g}[RCH(ONH_2)COOR']$; $\Delta H^0_{f,c} = \Delta H^0_{f,c}[RCH(ONH_2)COOR'·HCl]$; ΔH^0_r = enthalpy of reaction; all enthalpy values in kJ mol^{-1}.

[b] Values with an asterisk correspond to the radical isomerization.

[c] Values in parentheses correspond to the alkyl (R') transfer.

[d] The values express fraction of P_0, where P_0 is the atmospheric pressure.

following values of group parameters were used. The value of C–(C)(CO)(H)(O) was found to be −16.0 kJ mol^{-1} using the heat of formation [70] and heat of sublimation [71] of crystalline 2-hydroxypropanoic acid and taking other group parameters from ref. 69. For $C–(CO)(H)_2(O)$ we assumed a value of −32.3 kJ mol^{-1} from the comparison of differences of appropriate group parameters in the series of 1-aminocarboxylic acids [69,72,73]. Similarly, the value of $C–(H)_3(O)$ was found to be −58.2 kJ mol^{-1} by combining the most recent values of heats of formation of several methyl esters [72] with adequate group parameters from ref. 69. Taking other group parameters from the original work of Benson and coworkers [69] we calculated the values for $\Delta H^0_{f,g}$ [$RCH(ONH_2)COOR'$] listed in Table 2. Values for the enthalpy of formation of crystalline hydrochlorides were estimated from the thermochemical cycle analogous to that for ammonium and alkanaminium chlorides [74], assuming for $\Delta H^0_{f,g}$[HCl] a value equal to

-92.3 kJ mol^{-1} [75], and for the heat of sublimation a value equal to 175 kJ mol^{-1}. The latter is the mean of several values for heats of sublimation derived for alkanaminium chlorides [74]. Values for $\Delta H^0_{f,c}$[RCH(ONH$_2$)COOR′ · HCl] are also listed in Table 2.

To calculate the enthalpy changes for reactions (1) and (2), and for the radical cross-combination process the following values of heats of formation of reactants were used (in kJ mol^{-1}): $\Delta H^0_{f,g}$[CO] = -110.5 [72,75]; $\Delta H^0_{f,c}$[NH$_4$Cl] = -314.4 [75]; $\Delta H^0_{f,c}$[MeNH$_3$Cl] = -287.6 (mean from values reported in refs. 64, 72, 74); $\Delta H^0_{f,c}$[EtNH$_3$Cl] = -312.3 [74]; $\Delta H^0_{f,g}$[H] = 218.0 [41,64,75]; $\Delta H^0_{f,g}$[Me$^{\cdot}$] = 145.3 (mean of values reported in refs. 41, 53, 55, 57, 64, 72, 75); $\Delta H^0_{f,g}$[Et$^{\cdot}$] = 112.3 (mean of values listed in refs. 41, 53, 55, 57, 62, 64); $\Delta H^0_{f,g}$[*n*-Bu$^{\cdot}$] = 69.8 (mean of values reported in refs. 53–55); $\Delta H^0_{f,g}$[$^{\cdot}$COOH] = -240.0 (mean of values reported in refs. 76,77); $\Delta H^0_{f,g}$[$^{\cdot}$COOMe] = -161.1 [49,64]; and $\Delta H^0_{f,g}$[$^{\cdot}$COOEt] = -188.6 (estimated by the group additivity method [69]). For other radicals we used values listed in the previous section. Values for enthalpy of formation of gaseous and solid carboxylic acids and their esters were taken from ref. 72. Some of these have not been reported and we estimated them using the additivity scheme [69,71]. The values are (in kJ mol^{-1}): $\Delta H^0_{f,g}$[EtCOOMe] = -431, $\Delta H^0_{f,g}$[*i*-BuCOOH] = -497, $\Delta H^0_{f,g}$[*t*-BuCOOH] = -502, and $\Delta H^0_{f,c}$[BzCOOH] = -418. The derived values for the heats of reactions are listed in Table 2.

To facilitate further discussion we also estimated vapour pressures for reaction products at the onset of decomposition ($T_{0.01}$) and at temperatures corresponding to the first strong peak in DTG (T^1_{DTG}). Vapour pressures of ammonium or alkanaminium chlorides were evaluated using data from ref. 74. Vapour pressures of carboxylic derivatives were estimated from the Clausius–Clapeyron equation using temperatures corresponding to the boiling points from ref. 64 and heats of vaporization from ref. 72. Whenever the latter data were not available we estimated them using the additivity scheme [71]. Values of vapour pressures are listed in Table 2.

5. Final remarks

The derived enthalpies for reaction (2), from now on referred to as ΔH^0_r(2), are all positive. This means that the process can be initiated only by enhancing the energy of the system. If, indeed, reaction (2) describes the primary step in the thermal decomposition of the compounds studied the derived ΔH^0_r(2) values can be considered as an activation barrier for the process. The existence of a kinetic barrier for thermolysis seems to be indisputable since all the compounds studied are thermodynamically unstable relative to the products of the thermal decomposition. This follows from the negative value of enthalpy change for reaction (1). Therefore, without the existence of such a barrier 2-aminooxyacids, or their derivatives would

rearrange simultaneously to thermodynamically more stable systems. The enthalpy change for reaction (2) corresponds very well to the energy of the O–N bond (section 2). This coincidence may, of course, be fortuitous, but nevertheless tends to support the reaction model proposed earlier. $\Delta H_r^0(2)$ values for esters are ca. 45 kJ mol^{-1} higher than those for acids. However, they are comparable to those for acids if R′ transfer is assumed to occur as the primary step. This rearrangement would lead to the formation of carboxylic acids upon decomposition of esters, and this is actually confirmed experimentally.

Decomposition of the compounds commences when the temperature reaches a certain threshold value. Once the compounds start to decompose secondary processes occur. Among these processes radical combination reactions are highly exothermic (Table 2). Reaching an appropriate temperature level the system is capable of drawing enough energy from the environment to cause the decomposition of molecules. Therefore, the whole enthalpy change corresponding to the radical combination must be released in the form of heat. Indeed, distinct exothermic effects are always observed in the DTA curves of the compounds studied. This process may cause a local increase of temperature and an acceleration of the decomposition process. The effect described above is particularly pronounced upon thermolysis of aminooxyacetic acid hydrochloride (Fig. 2A) and is responsible for the unique thermal behaviour of the compound. It can result from the fact that the activation barrier and the amount of heat released during radical combination both reach relatively high values. A similar phenomenon, named "self-burning", has also been observed during thermal decomposition of hydrazine hydrochloride [78].

Carbon monoxide formed upon thermolysis is instantaneously transferred to the gas phase since the temperatures for the process always far exceed the boiling point of the compound. On the other hand, ammonia or amine hydrochlorides remain mostly in the condensed phase upon the first step of decomposition (Table 2). The derivatives of carboxylic acids formed may occur both in gaseous and condensed phases (Table 2). However, for the majority of compounds studied they are transferred to the gas phase instantaneously with the decomposition process. An exception is phenylacetic acid which volatilizes at higher temperatures [79]. Ammonia or amine hydrochlorides volatilize usually after the decomposition is completed [74]. This process is seen as a second stage on TG and DTG curves. All dependencies discussed above remain in qualitative agreement with experimental thermoanalytical curves.

The complete description of the thermal decomposition of 2-aminooxyacids and their derivatives is, undoubtedly, much more complicated than is shown in this work. Nevertheless, our approach forms a useful framework in which to consider the thermochemistry of this group of compounds.

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