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THERMAL ANALYSIS OF 1-HYDROXIETHYLIDENEDIPHOSPHONIC ACID AND ITS SALTS

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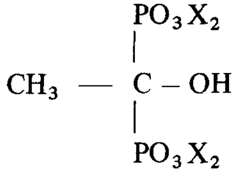
1-Hydroxyethylidenediphosphonic acid and its tetrasubstituted Li, Na, K, Rb, NH_4, Ca and Ba salts were synthesized and their thermal behaviour was studied under non-isothermal conditions by simultaneous TG-DTG-DTA at 20–1000 °C. The following thermal transformations were observed: loss of crystallization water, melting in the case of the acid, and intramolecular dehydration in the case of the salts, leading to the corresponding unsaturated derivatives. From the free acid, its acidic salts and the neutral ammonium salt, long-chain polycondensates are formed through intermolecular dehydration.

1-Hydroxyethylidenediphosphonic acid (HEDPA) is extensively used in many fields of application, e.g. washing-powder manufacture, electroplating, water treatment, metal surface treatment, and as a useful reagent in chemical analysis. It is also an important intermediate in organophosphorus chemistry, for the manufacture of pesticides and herbicides, and also as a fire-retardant in the plastics industry.

Due to their chemical structure HEDPA and its salts show very strong sequestering properties:



$$CH_3 - \overset{\overset{PO_3X_2}{|}}{\underset{\underset{PO_3X_2}{|}}{C}} - OH$$

where:

X = H in HEDPA, and

X = one equiv. of metal in the salts

Owing to the presence of the two phosphonic and one hydroxy groups, HEDPA (like its derivatives) is a polydentate ligand which forms soluble complexes with most polyvalent metal ions, and selectively precipitates many cations from acid solutions, e.g. calcium, magnesium, thorium (IV), scandium, uranium (VI), etc. [1]. Therefore, HEDPA and its salts are interesting from both technological and analytical aspects.

No work dealing with the thermal behaviour of HEDPA has been found in the literature [1–6]. To assess the usefulness of HEDPA and its salts at

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elevated temperatures, it is important to know their thermal stabilities. A study of the thermal behaviour of HEDPA and some of its salts (Li, Na, K, Rb, NH_4, Ca and Ba) was therefore undertaken as part of a systematic investigation on diphosphonic acids [7].

Experimental

Preparation of HEDPA and its salts

1-Hydroxyethylidenediphosphonic acid was prepared in the direct reaction of phosphorus trichloride with acetic anhydride [8]. The HEDPA obtained was purified by multiple crystallization from aqueous solution. Chemical analysis proved that under these conditions HEDPA is a monohydrate. The tetrasubstituted salts of HEDPA were obtained by total neutralization of the acid with the appropriate metal or ammonium hydroxide in 10–40% aqueous solution, depending on the nature of the salt. The water-soluble salts (Li, Na, K, Rb and NH_4) were precipitated by adding methanol, while the others (Ca and Ba) precipitated immediately. The chemical compositions of the products were established by means of chemical analysis. Before the thermal analysis, samples were carefully powdered and dried in vacuum at 60° for 12 h.

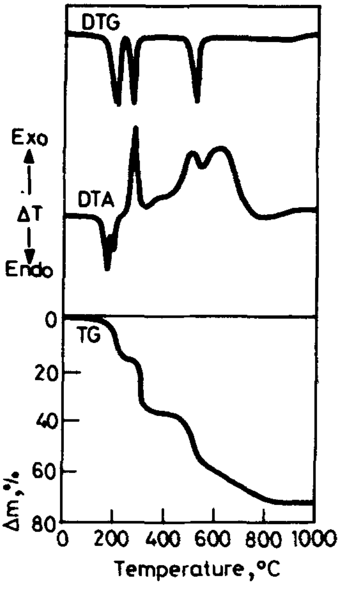

Fig. 1 Thermal curves of 1-hydroxyethylidenediphosphonic acid

Thermal measurements

TG, DTG and DTA curves were recorded simultaneously, using a Paulik-Paulik-Erdey OD–102 derivatograph. Samples (200 mg) were heated in a ceramic crucible in the temperature range 20–1000° at a constant heating rate of 10 deg $\min^{-1}$. A controlled dynamic atmosphere of air ($2 \cdot 10^4$ cm^3 h^{-1}) was used in the furnace.

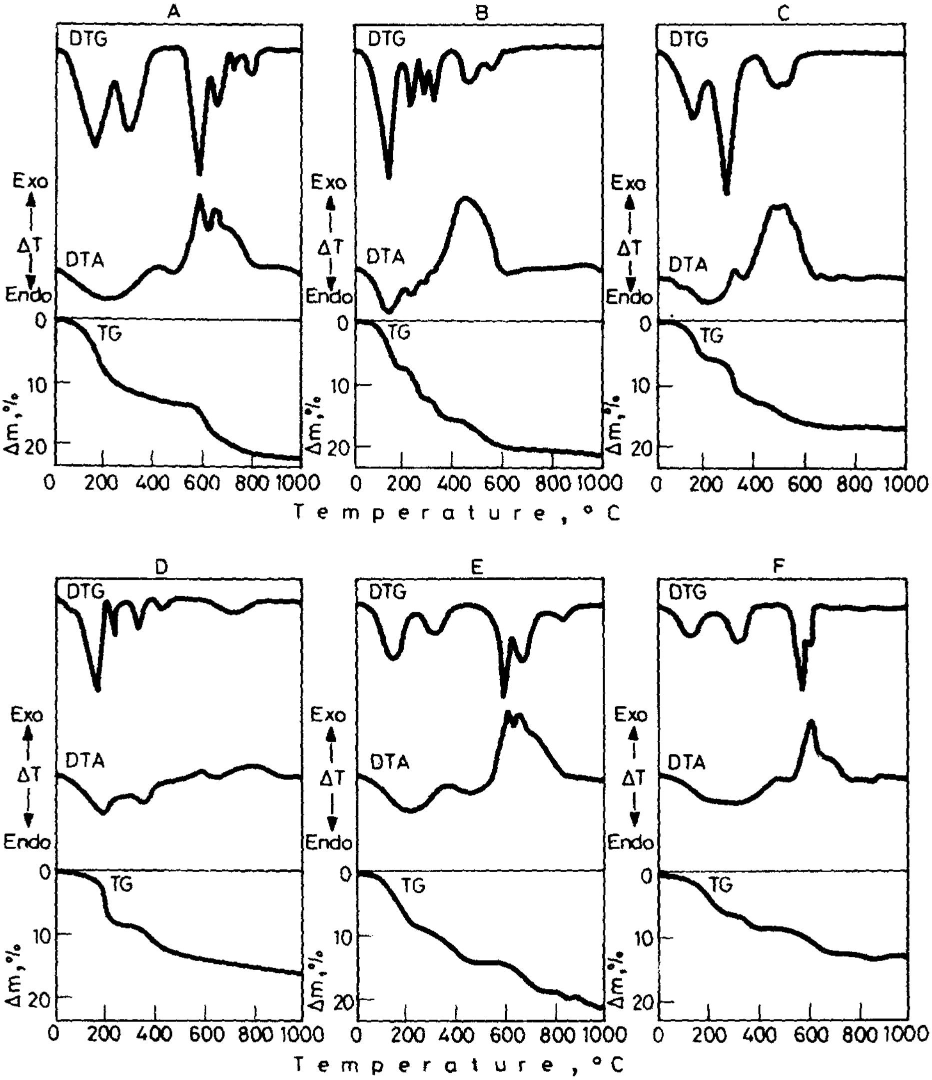

Fig. 2 TG-DTG-DTA curves of HEDPA salts: Li (A), Na (B), K (C), Rb (D), Ca (E) and Ba (F).

Table 1 The main thermal transformations of HEDPA and its salts in the range 20–1000 °C (in air)

Compound	DTG peak temp, °C	TG wt. loss %	Total wt. loss up to 1000 °C, %	DTA peak temp, °C	Thermal effect	Process
$HEDPA\cdot H_2O$	–	–		180	endo	melting of monohydrate
	200	16.1		202	endo	$-H_2O$ cryst.
	263	17.9		265	exo	condensation
	515	16.0		515	exo	polycond.
			72.5			
Li salt	170	9.1		200	endo	$-H_2O$ cryst.
	327	4.9		330	endo	dehydration C=C form.
	583	2.5		583	exo	polymn + decomp.
	656					oxidative
	730	4.95		630–855	exo	
	792					destruc.
			23.2			
Na salt	170	9.5		180	endo	$-H_2O$ cryst.
	230	2.8		240	endo	$-H_2O$ cryst.
	293	1.75		295	endo	$-H_2O$ cryst.
	313	1.0		315	endo	dehydration C=C form.
	450	5.5		420–580	exo	Polymn. + oxid. destr.
	550					
			22.1			
K salt	160	9.0		180	endo	$-H_2O$ cryst.
	300	7.3		300	endo	dehydration C=C form.
	495	3.9		500	exo	oxid. destr.
			17.1			
Rb salt	180	6.3		190	endo	$-H_2O$ cryst.
	255	3.0		290	endo	$-H_2O$ cryst.
	350	3.4		–	endo	dehydration C=C form.
	430	3.1		440	exo	oxid. destr.
	690			700		
			16.5			
NH_4 salt	200	12.2		230	endo	$-H_2O$ cryst.
	240	3.1		240	endo	$-H_2O$ cryst.
	300	5.9		340	endo	NH_3 envolv.
	400	5.5		420	endo	polycond.
	470	3.9		470	endo	decomp.
	680	11.3		680	exo	oxid. destr.
			51.2			

Compound	DTG peak temp, °C	TG wt. loss %	Total wt. loss up to 1000 °C, %	DTA peak temp, °C	Thermal effect	Process
Ca salt	164	9.0		180	endo	$-H_2O$ cryst.
	317	4.75		320	endo	dehydration $C=C$ form.
	600	2.95		600	exo	oxid. destr.
	660	2.6		660	exo	oxid. destr.
			22.7			
Ba salt	150	4.4		160	endo	$-H_2O$ cryst.
	330	3.1		320	endo	dehydration $C=C$ form.
	570	4.3		570	exo	oxid. destr.
	600	0.4		610	exo	oxid. destr.
			12.6			

Results and discussion

The characteristics of thermal transformation of the compounds (Table 1) were determined on the basis of the TG, DTG and DTA traces of HEDPA (Fig. 1) and its salts (Fig. 2).

The data in Table 1 reveal clear differences in thermal behaviour between HEDPA and its salts. Melting is observed only in the case of HEDPA monohydrate. The endothermic DTA peak occurs at 180°; no corresponding DTG peak is visible at this temperature. This phase change is followed by the loss of crystallization water at 200°. The transformation at 263° is connected with intermolecular dehydration, and in this stage oligocondensates are formed. Above ca. 500°, a deep polycondensation takes place, combined with PH_3 liberation and total oxidative destruction.

The ammonium salt decomposes in a manner similar to the acid, but the polycondensation is accompanied by NH_3 elimination. For both HEDPA and its ammonium salt, intramolecular dehydration leading to formation of the carbon double bond was not observed, whereas for the other tetrasubstituted salts tested this reaction was found.

All the salts examined contained water of crystallization and therefore most of the endothermic peaks (in the first part of the TG-DTA curves) are connected with the loss of this water. When this process is finished, the double bond is formed with the intramolecular elimination of H_2O molecules. The temperature of this process is only slightly influenced by the nature of the cation; it varies from 300° to 350°. The stability region of the

C=C compound, appearing as a plateau in the TG curve, clearly depends on the cation. In the case of the calcium and barium salts, the unsaturated derivatives are stable even up to 600 and 570°, respectively. However, oxidative destruction was recorded above 500° in the other cases. Chemical analysis of the glassy substances left as a solid residue in the crucible demonstrated the presence of polyphosphates.

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Zusammenfassung — 1-Hydroxyethyldiphosphonsäure und ihr Li-, Na-, K-, Rb-, NH_4-, Ca- und Ba-Salz wurden dargestellt. Ihr thermisches Verhalten wurde durch simultane TG-DTG-DTA unter nichtisothermen Bedingungen bei 20–1000 °C untersucht. Folgende thermische Umwandlungen wurden beobachtet: Verlust von Kristallwasser, Schmelzen (nur bei der freien Säure), intramolekulare Wasserabspaltung (nur bei den Salzen) zu ungesättigten Verbindungen. Die freie Säure, die sauren Salze und das neutrale Ammoniumsalz bilden unter intermolekularer Wasserabspaltung langkettige Polykondensate.

РЕЗЮМЕ — Синтезированы 1-оксиэтилидендифосфоновая кислота и ее четырехзамещенные соли лития, натрия, калия, рубидия, аммония, кальция и бария. Термическое поведение их было изучено неизотермически в температурном интервале с помощью совмещенного метода ТГ—ДТГ и ДТА. Установлены такие термические превращения, как потеря кристаллизационной воды, плавление свободной кислоты и внутримолекулярная дегидратация солей, приводящая к образованию соответствующих ненасыщенных соединений. В случае своборной кислоты, ее кислых солей и нейтральной аммониевой соли, внутримолекулярная дегидратация приводила к образованию длинноцепочечных поликонденсатов.