USE OF THERMAL ANALYSIS IN THE SYNTHESIS OF VINYLIDENEDIPHOSPHONIC ACID
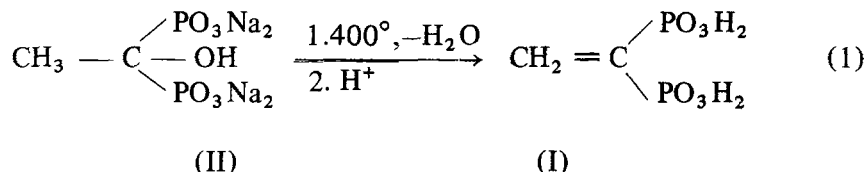
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Simultaneous TG–DTA was applied to establish the optimum conditions for the synthesis of vinylidenediphosphonates via the intramolecular dehydration of 1-hydroxyethylidenediphosphonate salts (Li, Na, K, Rb, NH₄, Ca and Ba). The tested salts underwent water elimination at different temperatures. Consequently, they are of different values for the synthesis of vinylidenedi phosphonates. The dibarium salt proved to be the best for this purpose, whereas the tetrammonium salt can not be used because of its uncontrolled thermal decomposition. The kinetic parameters do not reveal any influence of the metal cation on the intramolecular dehydration process.

Vinylidenediphosphonic acid (VDPA) and its derivatives, especially its salts and esters, have found use as sequestering agents [1, 2], in the development of polymeric flame retardants [3, 4], and in certain pharmaceutical applications [5, 6]. Moreover, this acid may be conveniently used as a monomer to obtain cation-exchange resins with $-PO_3H_2$ groups. These phosphonic cation-exchangers owe their importance in analytical and technological applications to their high selectivity [7].

Though a few methods of preparation of VDPA (I) have been described [1–6,8], VDPA is currently prepared via the thermal dehydration of tetra-sodium 1-hydroxiethylidenediphosphonate (II) at high temperature according to Eq. (1):

$$CH_3 - C \overset{\nearrow PO_3Na_2}{\underset{\searrow PO_3Na_2}{-}} OH \quad \xrightarrow[\text{2. } H^+]{1.400°,\,-H_2O} \quad CH_2 = C \overset{\nearrow PO_3H_2}{\underset{\searrow PO_3H_2}{}} \tag{1}$$

$$\text{(II)} \qquad\qquad\qquad \text{(I)}$$

Our initial attempt to apply the above method directly for the conversion of various neutral salts (Li, Na, K, Rb, NH₄, Ca and Ba) of 1-hydroxyethylidenediphosphonic acid (HEDPA) to vinylidendiphosphonates presented many practical problems. This disadvantages of this procedure include the need for precise temperature control during the dehydration step, and

lengthy and time-consuming separation and purification processes. Thus, it is impossible to obtain the final product in a good yield because the post-reaction mixture contains unreacted HEDPA salt and some thermal decomposition products.

The purpose of our investigations was to apply thermal analysis to the process of intramolecular dehydration of neutral salts of HEDPA. In order to establish the optimum dehydration temperatures for these seven salts, preliminary thermogravimetric runs were made. Since these gave interesting results, and a literature search showed that no work had so far been published on the thermal analysis of these compunds, simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) studies were carried out. The TG traces were also subjected to mathematical treatment and kinetic parameters for the intramolecular dehydration of the HEDPA salts were evaluated.

Experimental

Preparation of the samples

The tetrasubstituted salts (Li, Na, K, Rb, NH_4, Ca and Ba) of HEDPA were prepared by direct total neutralization of HEDPA, obtained according to [9], with equivalent amounts of the appropriate hydroxides. Methanol was added to the aqueous solution to precipitate the salt. After crystallization, products were filtered off by suction, washed with methanol and dried in vacuum 60° for 24 h. All salts were white crystalline solids and no additional purification process was required. The purities and degrees of substitution of the salts were checked by elemental analysis for P and by atomic absorption spectrophotometry for metals. In the case of the ammonium salt, the nitrogen content was determined by means of the Kjeldahl method.

Thermal analysis of HEDPA salts

An OD–102 MOM derivatograph (Budapest) was used, and TG, DTG and DTA curves were recorded simultaneously. Thermal analysis was performed over the temperature range 20–1000°. Powdered samples (200 mg) were heated in a ceramic crucible at a rate of 10 deg·min^{-1}. A controlled dynamic atmosphere of air (20 l·h^{-1}) was used in the furnace.

Synthesis of VDPA

To obtain the VDPA salts, and then free VDPA, samples (1 g) of HEDPA salts were heated in a controlled-temperature furnace. Each salt was dehydrated at the appropriate temperature assigned earlier on the basis of the TG-DTG-DTA results.

For determination of the degree of conversion, the thermally treated products were analysed by bromometry. In the same way, the time dependence of the dehydration process was established. Detailed results in this respect will be published elsewhere.

Treatment of thermoanalytical data

From the TG and DTA curves, the following data were determined: T_i, T_m and T_f (the initial, maximum and final temperatures of the TG-DTG peak of the dehydration reaction). The order of reaction n and the activation energy E were evaluated according to the Horowitz–Metzger [10] and Coats-Redfern [11] methods.

Results and discussion

DTG and DTA curves for these HEDPA salts are presented in Fig. 1. It can be seen that several thermal effects could be observed for all salts. These effects correspond to the following transformations:
— the loss of crystallization water,
— intramolecular dehydration, combined with formation of the carbon double bonds,
— thermal decomposition of the VDPA salts formed.

The endothermic transformations in the temperature range 80–300° are connected with the loss of crystallization water. Depending on the nature of the salt, this process occurs in one or more stages. This conforms with the number of hydrate water molecules in the given HEDPA salt. The degree of hydration of each salt was earlier established via chemical analysis.

The endothermic processes in the range up to 380° correspond to the loss of intramolecular water when the formation of VDPA salts takes place. In the case of the sodium and rubidium salts, the DTG and DTA peaks corresponding to the crystallization and intramolecular water loss overlap. This resulted in unfavourable values of the equilibrium constants for synthesis of the VDPA salts.
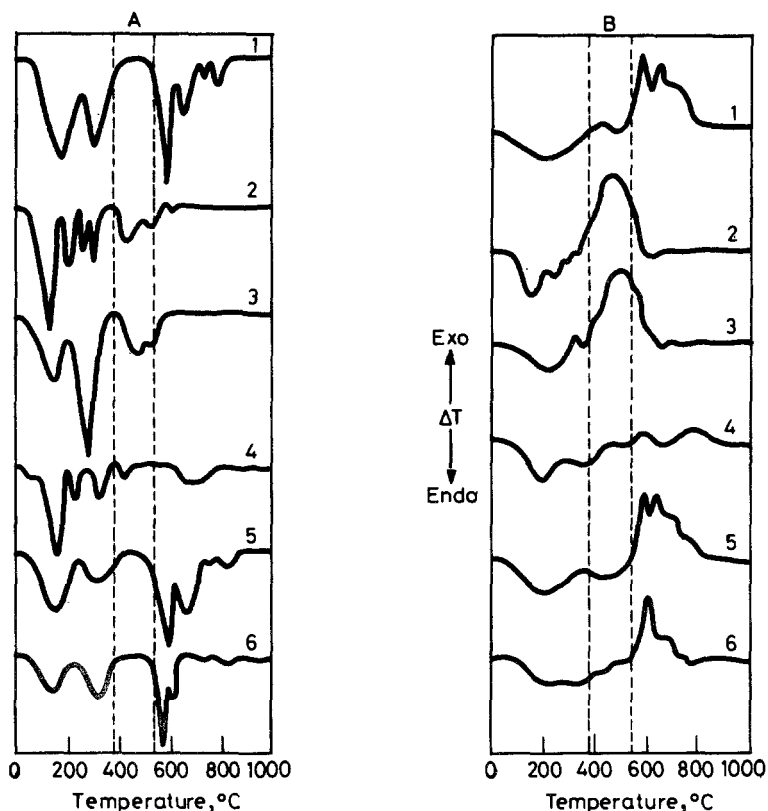
Fig. 1 DTG curves (A) and DTA curves (B) of 1-hydroxyethylidenediphosphonic acid salts: 1-Li, 2-Na, 3-K, 4-Rb, 5-Ca, 6-Ba.

Above 380° the VDPA salts display different behaviour: the Li, Ca and Ba salts are thermally stable up to ca. 530°, while a strong exothermic peak is seen for the other salts. This is connected with the uncontrolled oxidative destruction of the VDPA salt formed.

The kinetic parameters were calculated for the intramolecular dehydration stage. When the Horowitz–Metzger and Coats-Redfern equations were used, typical plots were obtained. From the slopes of the straight lines, the values of E were calculated (Table 1).

It is seen from Table 1 that the activation energy of the main transformation is practically independent of the nature of the cation, while the reaction order is $n = 1$ for monovalent cation salts and $n = 3/2$ for divalent cations. The values of E determined with the Horowitz–Metzger method are in all cases higher than those obtained with the Coats-Redfern method, but the results agree within the limits of error.

Table 1 Thermal data and kinetic parameters for the stage of VDPA salt formation

Cation in salt	Intermolecular dehydration		Temp. range of VDPA salt stability	Order of reaction n	E, kJ mol^{-1}	
	temp. range °C	DTG peak, °C			H–M	C–R
Li	280–370	327	370–555	1	177	169
Na	285–325	313	–	1	172	157
K	270–330	300	330–355	1	169	154
Rb	320–380	350	–	1	189	181
Ca	280–370	317	370 550	3/2	175	167
Ba	285–365	330	365–530	3/2	180	171

References

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Zusammenfassung — Simultane TG-DTA wurde eingesetzt, um die optimalen Bedingungen für die Synthese der Vinidylidendiphosphonate durch intramolekulare Wasserabspaltung aus den 1-Hydroxiethylidendiphosphaten des Li, Na, K, Rb, NH₄, Ca und Ba zu ermitteln. Aus den untersuchten Salzen wurde das Wasser bei verschiedenen Temperaturen abgespalten, sie sind daher unterschiedlich brauchbar zur Synthese der Vinylidenphosphonate. Das Bariumsalz erwies sich als am geeignetsten, während das Tetraammoniumsalz wegen seiner unkontrollierten thermischen Zersetzung ungeeignet ist. Die kinetischen Parameter der intramolekularen Wasserabspaltung zeigen keinen Einfluss des vorhandenen Metallkations.

РЕЗЮМЕ — Совмещенный метод ТГ и ДТА был использован для определения оптимальных условий синтеза винилидендифосфонатов через стадию внутримолекулярной дегидратации 1-оксиэтилидендифосфонатов лития, натрия, калия, рубидия, аммония, кальция и бария. Выделение воды для всех солей происходит при различных температурах. Следовательно, они по разному могут быть использованы для синтеза винилидендифосфонатов. Бариевая соль наилучшим образом подходит для этой цели, тогда как аммониевая соль, вообще, не может быть использована для синтеза, вследствии ее неконтролируемого термического разложения. Кинетические параметры показали, что процесс внутримолекулярной дегидратации не затрагивается природой катиона металла.