

# KINETICS OF THERMAL DECOMPOSITION OF ALKALINE PHOSPHATES

T. Vlase\*, Gabriela Vlase and N. Doca

West University of Timișoara, Faculty of Chemistry–Biology–Geography, Str. Pestalozzi No. 16, Timisoara 300115, Romania

The thermal behavior of  $\text{KH}_2\text{PO}_4$ ,  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  under non-isothermal conditions using TG method with different heating rates was studied. The values of the reaction rate were processed by means of Friedman's differential-isoconversional method. A dependence of the activation energy *vs.* conversion was observed. Therefore a procedure based on the compensation effect (suggested by Budrugeac and Segal) was applied. A less speculative data processing protocol was offered by the non-parametric kinetics method suggested by Serra, Nomen and Sempere.

Three steps were observed by non-isothermal heating: a dehydration, a dimerization and a polycondensation. The differences in the intimate reaction mechanism are determined by the initial number of water molecules.

**Keywords:** compensation effect, isoconversional methods, non-isothermal kinetics, non-parametric kinetics (NPK)

## Introduction

In the last years the thermal analysis is more and more used for food safety [1]. The thermal stability of food additives in connection with the thermal processing of foods is one of the major fields of interest.

In this paper, the non-isothermal kinetics of thermal decomposition of  $\text{KH}_2\text{PO}_4$ ,  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  was studied. The main use of these salts in the food industry is as buffer and/or neutralization reagents.

## Experimental

The studied compounds  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  (**I**),  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (**II**) and  $\text{KH}_2\text{PO}_4$  (**III**) were analytical grade.

The thermogravimetric (TG) and derivated TG (DTG) curves were determined with a Perkin-Elmer TGA7 Thermobalance in the range 50–500°C, with heating rates 5, 7, 10 and 12 K min<sup>-1</sup>, under dynamic nitrogen atmosphere.

## Results and discussion

Examples of the TG and DTG diagrams of the studied samples are presented in Fig. 1.

The TG curves corresponding to the three studied compounds exhibit some common characteristics:

- till 100°C a mass loss due to the humidity (unimportant for our further discussions)
- a step A corresponding to the loss of the crystallization water

- a step B corresponding to a dimerization with water loss
- a step C corresponding to a polycondensation, also accompanied by water loss

In Table 1 these TG data are systematized.

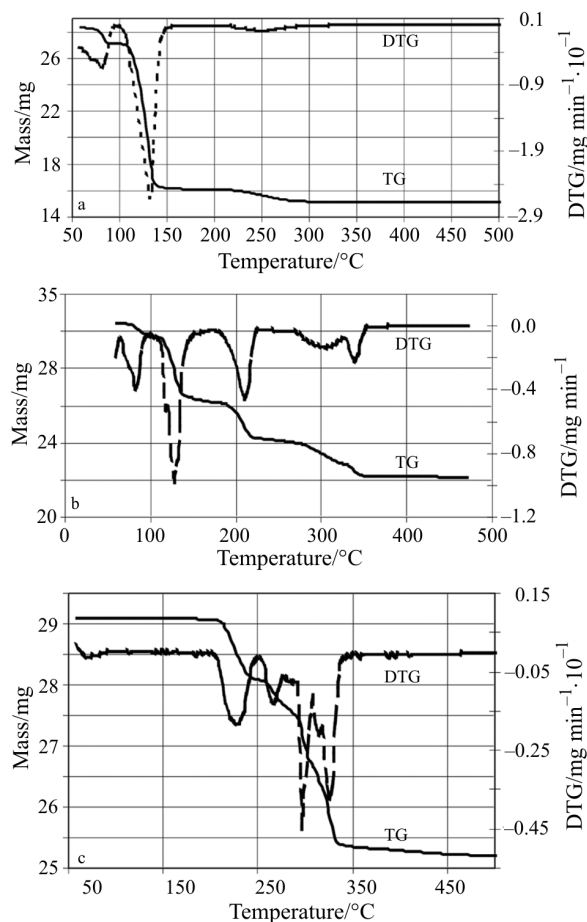
By compound **I**, the step A has a significant contribution to the total water loss. The difference between the determined loss for 12 water molecules and the calculated ones is probably due to a partial dehydration to a dihydrate (process possible at room temperature). The step B corresponds to the dimerization to pyrophosphate  $\text{Na}_4\text{P}_2\text{O}_7$ .

The decomposition of compound **II** is more complex. Step A is well defined by the TG curves, and the determined mass loss is in a good agreement with the calculated values. The dimerization step B is good separated and also a very good agreement between  $\Delta M_d$  and  $\Delta M_c$  values is remarked. At temperatures up to 560°C, a polycondensation of the dimers take place.

This corresponds to step C, is rather difficult to separate on the TG curves. The water loss of the global condensation process depends on the condensation degree *n*, as is depicted in Fig. 2. For the compound **II**, the upper limit of the water loss from the entire condensation process is  $\Delta M_c=15\%$ , in a very good agreement with the determined values for the both B and C steps.

In the case of compound **III** there are some differences in comparison with the sodium salts **II**. Being an anhydrous salts, the step A is absent. But the remarkable difference is by transition from step B to step C. The potassium salts is more active. The dimerization

\* Author for correspondence: tvlase@cbg.uvt.ro



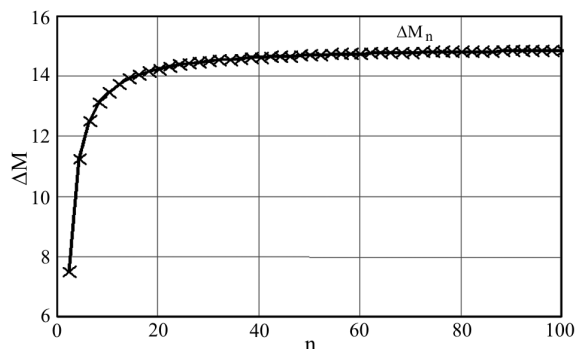
**Fig. 1** The TG and DTG curves obtained for a heating rate of  $5 \text{ K min}^{-1}$  a – I, b – II and c – III

step starts at a lower temperature and is not well separated from step C; it means that the polycondensation process is started before the dimerization is finished. This is the explanation of the differences of  $\Delta M_d$  and  $\Delta M_c$  for the step B. But the sum of  $\Delta M_d$  for the B and C steps is in a very good agreement with the maximum  $\Delta M_c$  value of 13.2% for the entire polycondensation process (from a diagram similar with Fig. 2).

Since only steps A and B are well separated and in a rather good agreement with the theoretical suggested processes, these oneself should be kinetically analyzed.

**Table 1** Determined and calculated mass loss at four heating rates

Compound	Formula	Step	Determined mass loss, $\Delta M_d/\%$ at heating rate, $\beta/\text{K min}^{-1}$				Calculated mass loss, $\Delta M_c/\%$
			5	7	10	12	
I	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	A	43.4	43.9	43.7	44.2	60.33
		B	6.3	5.9	5.7	6.3	6.33
II	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	A	11.2	12.2	11.7	11.5	13.0
		B	7.2	7.1	7.4	7.3	7.5
		C	7.4	7.5	6.9	7.0	7.5
III	$\text{KH}_2\text{PO}_4$	B	4.9	5.4	5.4	5.8	6.6
		C	7.8	7.6	7.6	7.2	6.6



**Fig. 2** Water loss  $\Delta M$  of the global condensation process vs. condensation degree  $n$

### Kinetic analysis

We begin the analysis with Friedman's differential isoconversional method [2], using the relationship:

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \quad (1)$$

where  $\alpha$  – the conversion degree,  $\beta$  – heating rate,  $A$  – the pre-exponential factor and  $E$  – the activation energy in sense of Arrhenius equation.

With  $\alpha$  constant and various heating rates, the plot  $\ln[\beta(d\alpha/dT)]$  vs.  $1/T$  should be linear and from the slope, the value of activation energy should be calculated.

In Table 2, the  $E$  vs.  $\alpha$  values are systematized. Unfortunately, an important variation of the activation energy with the degree of conversion is observed, so that these values of  $E$  are inadequate for discussions about reaction mechanism.

Therefore we continue our analysis with the method proposed by Budrugaec and Segal [3–5] and successfully used in our previous note [6, 7]. This method is based on the following assumptions:

- $E$  and  $A$  depends on the degree of conversion and are independent in respect of the heating rate
- $E$  and  $A$  are correlated through the compensation effect ( $CE$ )

$$\ln A = aE + b \quad (2)$$

**Table 2** Activation energy  $E$  (kJ mol<sup>-1</sup>) obtained by Friedman method for heating rates of 5, 7, 10 and 12 K min<sup>-1</sup>

Sample	$\alpha$								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	64.7	39.9	38.3	33.1	30.4	27.9	25.5	24.2	25.9
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	153.9	190.7	150.6	85.3	77.1	74.7	70.9	64.0	107.3
KH <sub>2</sub> PO <sub>4</sub>	117.8	111.2	105.0	105.6	104.4	101.6	107.5	113.5	129.7
NaH <sub>2</sub> PO <sub>4</sub>	257.9	224.3	223.9	187.3	153.4	124.7	109.3	104.7	89.2
Na <sub>2</sub> HPO <sub>4</sub>	61.9	60.9	54.3	48.4	38.3	30.2	25.3	29.5	56.6

**Table 3** Kinetic parameters according with Eq. (6)

Sample	$E_0$ /kJ mol <sup>-1</sup> (Eq. (3))	$E_1$ /kJ mol <sup>-1</sup> (Eq. (3))	$a \cdot 10^4$ /mol J <sup>-1</sup> (Eq. (2))	$b$ (Eq. (2))	$n$ (Eq. (5))	Corr. coeff.
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	40.5	11.6	2.732	-5.314	0.1	0.99987
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	162.2	76.6	3.003	-5.354	0.7	1
Na <sub>2</sub> HPO <sub>4</sub>	67.4	37.7	2.256	-6.038	0.7	1
NaH <sub>2</sub> PO <sub>4</sub>	253.9	111.8	2.558	-6.731	0.1	0.99996

- the dependence of  $E$  on the degree of conversion is given by

$$E = E_0 + E_1 \ln(1 - \alpha) \quad (3)$$

where  $E_0$  and  $E_1$  are constants

- the differential conversion function,  $f(\alpha)$  has the form

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

From the differential conversion function (9) it follows that

$$\ln[Af(\alpha)] = \ln A + n \ln(1 - \alpha) \quad (5)$$

and from the values of  $[Af(\alpha)]$  and  $\alpha$ , the values of  $\ln A$  corresponding to various values of  $n$  can be obtained. The plot of  $\ln A$  vs.  $E$  should be linear as required by the existence of compensation effect (Eq. (2)). The correct value of  $n$  will be that which gives a correlation coefficient closest to 1.00 for the straight line  $\ln A$  vs.  $E$ .

From Eqs (1)–(5) we obtain:

$$\ln \left( \beta \frac{d\alpha}{dT} \right) = \left( b + aE_0 - \frac{E_0}{RT} \right) + \left( aE_1 - \frac{E_1}{RT} + n \right) \ln(1 - \alpha) \quad (6)$$

The kinetic parameters according with Eq. (6) are systematized in Table 3.

With the terms  $E_0$  it is possible a less speculative discussion on the reaction steps.

A reasonable assumption is to consider that a dodecahydrate is easier dehydrated in comparison with a monohydrate, if the salts are similar. Indeed, the difference of  $E_0$  from 40.5 kJ mol<sup>-1</sup> (compound **I**) to 162.2 kJ mol<sup>-1</sup> (compound **II**) is illustrative.

By the dimerization step, the difference of reactivity between sodium and potassium dihydrogen phosphates, observed on the TG curves, is quantitatively represented by difference of the  $E_0$  values of 150 kJ mol<sup>-1</sup>.

In order to obtain more details on the kinetics of these two processes, the non-parametric kinetic (NPK) method by Serra, Nomen and Sempere [8–10] was used. This method is based on the assumption that the reaction rate can be expressed as a product of two independent functions,  $g(\alpha)$  and  $f(T)$ . The reaction rate  $d\alpha/dt$ , measured from several experiments at different heating rates,  $\beta$ , are organized as an  $i \times j$  matrix where the rows correspond to different degrees of conversion, from  $\alpha_1$  to  $\alpha_i$  and where columns correspond to different temperatures from  $T_1$  to  $T_j$ .

The NPK method uses the singular value decomposition (SVD) algorithm to decompose matrix  $A$ :

$$A = U(\text{diag } s)V^T \quad (7)$$

The vector  $u_1$  given by the first column of the matrix  $U$  is analyzed vs.  $\alpha$  (to determine the kinetic model) and the vector  $v_1$ , the first column of the matrix  $V$ , is analyzed vs.  $T$  (to determine the Arrhenius parameters). The singular value vector  $s$  takes into account the number of the steps of the reaction.

The elements of the matrix  $A$  were obtained from the DTG curves, by generating the surface of the reaction rates in a three-dimensional space ( $\alpha$ ,  $T$  and  $\beta(d\alpha/dT)$ ).

The data of the NPK analysis were presented in Tables 4 and 5. For the kinetic model, the Šesták–Berggren equation [11]

$$g(\alpha) = \alpha^m (1 - \alpha)^n \quad (8)$$

was proposed.

**Table 4** Kinetic parameters for the main process

	Sample	$\lambda/\%$	$E/\text{kJ mol}^{-1}$	$A/\text{min}^{-1}$	$n$	$m$
dehydration	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	99.3	27.7	$1.05 \cdot 10^3$	2/3	3.2
	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	92.2	51.9	$1.42 \cdot 10^6$	3/2	1
dimerization	$\text{Na}_2\text{HPO}_4$	84.9	89.9	$6.99 \cdot 10^7$	3/2	–
	$\text{NaH}_2\text{PO}_4$	90.5	65.4	$2.94 \cdot 10^6$	3/2	1
	$\text{KH}_2\text{PO}_4$	91.0	104.3	$1.57 \cdot 10^{10}$	1	–

**Table 5** Kinetic parameters for the secondary process

	Sample	$\lambda/\%$	$E/\text{kJ mol}^{-1}$	$A/\text{min}^{-1}$	$n$	$m$
dehydration	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	0.7	223.5	$14.25 \cdot 10^{28}$	1	1
	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	6.9	134.1	$1.19 \cdot 10^{16}$	–	2
dimerization	$\text{Na}_2\text{HPO}_4$	11.4	54.0	$1.57 \cdot 10^4$	2	2/3
	$\text{NaH}_2\text{PO}_4$	9.2	402.6	$3.47 \cdot 10^{41}$	–	1
	$\text{KH}_2\text{PO}_4$	8.7	435.3	$2.60 \cdot 10^{43}$	1	–

By the dehydration step A there is a single process ( $\lambda_1 > 90\%$ ). The trial with two singular values vectors  $s_1$  and  $s_2$  lead an insignificant  $\lambda_2 < 10\%$ . With the certitude of a single process we have the proof of an easier dehydration of the dodecahydrate: an activation energy approximately twice lower than monohydrate. But probably the intimate mechanism of dehydration is different, according to the different values of the  $n$  and  $m$  pairs. For  $n \cong 1$  and  $m \cong 1$  the process is controlled by branching nuclei interacting during their growth, whereas for  $n < 1$  and  $m > 1$  the chain growth and branching of nuclei is a later stage [11] of the dehydration step.

By the dimerization step also a single dominant process was found ( $\lambda_1 \cong 90\%$ ). Noticeable is that the three compounds exhibits three different mechanisms. The initial anhydrous compound **III** (no disturbed structure) seems to dimerize by a random nucleation with one nucleus on the individual particle ( $n=1$  and  $m=0$  [11]). This is also in connection with the superposition of steps B and C on the TG curve. By the corresponding sodium salts, the dimerization mechanism seems to be similar with the dehydration, probably because the loss of just one molecule of water does not deeply disturb the initial structure of the monohydrate.

For  $\text{Na}_2\text{HPO}_4$  the mechanism is only roughly by interpreted, because a serious disturbance and modification of the initial structure, after a loss of 12 molecules of water. Probably the process is phase-boundary controlled.

## Conclusions

- by the decomposition of alkaline phosphates under non-isothermal conditions, there are three separable steps: dehydration, dimerization and polycondensation. Only the first two are suitable for kinetic study

- the kinetic analysis reveals an important dependence of the activation energy on the degree of conversion
- from the three utilized methods, the NPK ones is able to offer kinetic parameters and details on reaction mechanism in a less speculative manner
- the intimate mechanism of dehydration and dimerization steps is strongly influenced by the number of water molecules of the crystallohydrate
- the temperature correspond to the beginning of the dimerization process can be a serious restriction criteria in use of the studied salts as food additives

## Acknowledgements

The authors are grateful to Professor Marek Maciejewsky (ETH Zürich) for the logistic support of this work.

## References

- 1 Proceedings of the 8<sup>th</sup> ESTAC Symp., Cap. 'Food, Pharmaceuticals and Life Science', Barcelona Aug. 2002, pp. 533–604.
- 2 H. L. Friedman, J. Polym. Sci., 6C (1965) 183.
- 3 P. Budrugaec and E. Segal, Thermochim. Acta, 260 (1995) 75.
- 4 P. Budrugaec and E. Segal, J. Therm. Anal. Cal., 62 (2001) 821.
- 5 P. Budrugaec and E. Segal, J. Therm. Anal. Cal., 66 (2001) 557.
- 6 T. Vlase, G. Vlase, A. Chiriac and N. Doca, J. Therm. Anal. Cal., 72 (2003) 839.
- 7 T. Vlase, M. Doca, G. Vlase and N. Doca, J. Therm. Anal. Cal., 72 (2003) 597.
- 8 R. Serra, R. Nomen and J. Sempere, J. Therm. Anal. Cal., 52 (1998) 933.
- 9 R. Serra, R. Nomen and J. Sempere, Thermochim. Acta, 316 (1998) 37.
- 10 R. Serra, R. Nomen and J. Sempere, J. Therm. Anal. Cal., 56 (1999) 843.
- 11 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.