CORRELATION BETWEEN ISOTHERMAL AND RISING TEMPERATURE EXPERIMENTS. THERMAL DECOMPOSITION OF DIAMMONIUM HYDROPHOSPHATE

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ABSTRACT

The thermal decomposition of diammonium hydrophosphate $(NH_4)_2HPO_4$ (DAHP) has been studied isothermally and in rising temperature experiments. The results of thermal analysis, confirmed by X-ray, chemical analysis and chromatography, show that $NH_4H_2PO_4$ is the product of the first step of DAHP decomposition. In isothermal experiments below 150°C, and using low heating rates (Φ), it is possible to stop the decomposition after the first step. Above 150°C, and for $\Phi > 5$ min^{-1}, the beginning of the $NH_4H_2PO_4$ decomposition and the occurrence of the liquid phase take place before the end of the first step. Kinetic parameters, A, E and g(α), determined in isothermic measurements, have been used for the theoretical calculations of TG traces in dynamic conditions. The knowledge of these parameters has helped in the correlation of the results of isothermal and dynamic experiments. Theoretical calculations have been confirmed by the experimental results.

INTRODUCTION

Thermal analysis is often used for the assessment of thermal stability of compounds, e.g. the determination of the temperature at which drying is possible, and, at the same time, there is no change of the stoichiometry of the reactant. It is well known that, in the case of reversible thermal decomposition, the experimental conditions, and, particularly, the partial pressure of the gaseous product(s) of the reaction will affect the temperature range of the decomposition. The controversies met in the literature concerning the initial temperatures of decomposition in rising temperature experiments are therefore unavoidable.

It is particularly important to determine thermal stability, or the temperature range of decomposition for the compounds which can start to decompose in the drying temperature range (usually 80–100°C), and the ones whose thermal decomposition takes place in intermediate stages, or may be disturbed by the occurrence of the liquid phase during decomposition.

Diammonium hydrophosphate (DAHP) is a compound whose thermal decomposition causes a number of controversies concerning the initial temperature of decomposition, the amount, stoichiometry and the temperature range for the intermediate stages. The purpose of this work was the examination of the first stage of DAHP decomposition, the determination of kinetic parameters of this reaction (apparent activation energy, E, Arrhenius pre-exponential factor, A, and the g(α) function describing the process investigated).

DAHP is one of the components of a chemical fertilizer containing a mixture of mono- and diammonium phosphates and ammonium sulphate. The drying temperature of this compound is important because an excessive temperature may cause the loss of ammonia and partial melting of the granulate, as well as its tendency to aggregate [1]. DAHP is also a raw material for the production of strontium–magnesium phosphates which, after the introduction of Sn^{2+} ions (being activators), are used as luminescent materials. Also, in this case, the knowledge of the temperature at which DAHP decomposition, combined with the evolution of ammonia begins may enable the careful selection of a drying temperature which does not affect the stoichiometry of the raw materials.

The first stage of the thermal decomposition of DAHP, taking place according to the reaction

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3 \tag{1}$$

depends, to a large extent, on the presence of NH_3 in the system. The change of the experimental parameters that increase the partial pressure of NH_3 in the system causes the shifting of the observed beginning of decomposition towards higher temperatures, after which further decomposition starts,

$$2NH_4H_2PO_4 \rightarrow NH_4H_3P_2O_7 + NH_3 + H_2O \tag{2}$$

$$2NH_4H_2PO_4 \rightarrow (NH_4)_2H_2P_2O_7 + H_2O \tag{3}$$
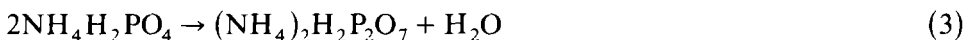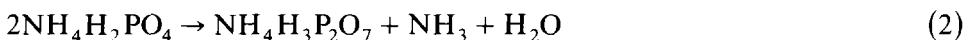
and the liquid phase occurs in the system.

In the literature there are controversial data concerning the temperature at which the beginning of the evolution of ammonia takes place.

According to Haldun et al. [2], at the heating rate of $4°C$ min^{-1}, the evolution of ammonia starts at a temperature of $120°C$. Duval and co-workers [3,4] have studied nearly 1000 analytical precipitates by the TG method. The objective has been to determine the temperature at which a precipitate is of stoichiometric composition and the temperature interval over which the precipitate is suitable for weighing. At the heating rate of $5°C$ min^{-1} (sample weight, 200 mg) the beginning of DAHP decomposition has been observed at the temperature of $111°C$.

Erdey and co-workers, in their work concerning the thermoanalytical properties of ammonia salts [5], have reported that the beginning of DAHP

decomposition occurred above 100°C (200 mg sample, heating rate 5°C min^{-1}). After the loss of ammonia the sample melts and diammonium dihydrogen pyrophosphate is formed by the removal of 1 mol of water.

The data presented by Erdey indicate that a number of decomposition processes take place simultaneously, and that it is impossible to distinguish one from another. The first stage of decomposition (the evolution of ammonia) passes in a continuous way into the second stage (the removal of 1 mol of water). The comparison of curves (DTA and DTG) points to the occurrence of the melting process in the temperature range between the end of the first and the beginning of the second stage.

The occurrence of the liquid phase has also been observed in the work of Nabiev et al. [6]. At the heating rate of 12–14°C min^{-1} the maximum endothermic effect ascribed to the melting of the partly decomposed DAHP was observed at a temperature of 185°C.

According to Pozin [7], DAHP starts to decompose in air at a temperature of 70°C, but Margulis [8], on the basis of isothermal measurements, is of the opinion that the beginning of decomposition takes place at a temperature of 140°C. The same temperature is also given in the work of Trzesniowski [1].

The equilibrium pressure of NH_3 over DAHP, determined by Warren [9] at a temperature of 80°C, equals 1.36 torr, at 100°C, 5.02 torr, at 109.3°C, 11.0 torr, at 116.9°C, 17.7 torr and at 125.4°C, 29.35 torr, respectively. Similar data are given by Zhdanov [10] (figures only, without numerical data). Taniguchi [11] determined the following values of the equilibrium pressure of ammonia (approximate values were determined on the basis of the diagram): 129°C, 61 torr; 142°C, 129 torr; 154°C, 239 torr.

The relationship $p_{NH_3} = f(T)$ and the value of the heat of decomposition given by Warren and Taniguchi (19.05 and 18.1 kcal mol^{-1}, respectively) enable the determination of the equilibrium pressure of NH_3 at room temperature on the basis of Clapeyron's equation. The value of $p_{eq}NH_3$ at a temperature of 300 K is 0.4 torr (according to Warren's data) or 0.2 torr (according to Taniguchi). Taking certain, arbitrarily chosen, values for the calculations ($p_{eq}NH_3$ at 300 K = 0.3 torr, m = 200 mg, reaction volume = 1000 cm^3), it is possible to point out that the partial pressure of NH_3, which is equal to the equilibrium pressure, can be obtained at a temperature of 300 K when the progress of decomposition reaches the value of $\alpha = 0.012$. It is obvious that the above calculations do not take the kinetics of the reaction into consideration: they only demonstrate that, from the thermodynamical point of view, the partial decomposition of DAHP may already take place at room temperature (which (see below) was confirmed experimentally).

In order to explain the discrepancies in the literature concerning the initial temperature of decomposition in dynamic conditions, and to find the correlation between the measurements carried out in isothermal and rising temperature conditions, a number of measurements of the thermal decomposition of DAHP were made using both experimental conditions.

EXPERIMENTAL

Isothermal measurements were carried out using the apparatus designed by the authors of this paper, which enables automatic registration of weight loss on an analytical balance with an accuracy of 0.1 mg. A 68 dm^3 heat chamber, ensuring temperature stability with an accuracy of $\pm$ 1°C, was used as the reaction volume: sample weight was $\approx$ 6.5 g. Measurements in non-isothermal conditions were made by means of a Derivatograph (heating rate, 0.6–20°C min^{-1}, a standard platinum crucible, $\approx$ 250 mg sample, static atmosphere of air) and a Mettler 2000 C thermoanalyser (heating rate, 1, 5 and 10°C min^{-1}, 50 mg sample, static atmosphere of air). $(NH_4)_2PO_4$ manufactured by POCH Gliwice, Poland, p.a., was used as a reactant.

Both the reactant and the product of the decomposition were examined after each measurement by means of X-ray powder analysis, paper chromatography and chemical analysis.

X-ray analysis was carried out on a Dron-20 diffractometer using Fe_α radiation. The NH_3 and P contents were determined by chemical analysis. NH_3 was determined by means of a commonly used method, consisting of heating the sample with NaOH solution and determining, by titration, the amount of ammonia evolved [12]. PO_4^{3-} was determined spectrophotometrically using the formation of a coloured complex with molybdenum–vanadium phosphoric acid [13].

One-dimensional ascending paper chromatography of a sample diluted in water was carried out according to the procedure elaborated by one of the authors of this paper [14]. This method enables confirmation of the presence of PO_4^{3-} and highly condensed phosphate anions.

The chemical analysis of DAHP showed full agreement with stoichiometric calculations (the obtained percentage weights of NH_3 and P were 25.71 and 23.44 % (theoretical values, 25.80 and 23.45%), respectively. X-ray data were in total agreement with test data (ASTM-card 9–391).

It was essential to analyse the product of the first stage of thermal decomposition in order to confirm the stoichiometry of this reaction according to equation (1).

Chemical analysis, X-ray powder analysis (full agreement of the product's diffractogram with ASTM 6–125 standard) and chromatography (the presence of PO_4^{3-} ions only) showed that, in the 60–140°C temperature range, $NH_4H_2PO_4$ was the only phase that was identified after the reaction. Weight loss, in agreement with reaction (1) was 12.89%.

The product of isothermal decomposition carried out at temperatures exceeding 150°C becomes, as the temperature increases, more and more molten, and the weight loss (exceeding 13%) indicates the beginning of the subsequent stage of decomposition.

(A) Isothermal measurements

The results of isothermal measurements are shown in Table 1, which presents percentage weight loss after the completion of the first stage of the thermal decomposition, time $t_{0.5}$, in which the progress of the decomposition $\alpha = 0.5$ was reached and the P content. Typical α–t relationships for three temperatures, 80, 110 and 135°C, are given in Table 2 and in Fig. 1.

Two methods were applied in order to determine the kinetic parameters:
Method 1. Called the reduced time method, it enables the determination of the kinetic parameters without the knowledge of the equation describing the mechanism of the process. This method [15–18] consists in the determination of the relationship between α and the reduced time t_r ($t_r = t/t_{0.5}$) for several temperatures. If the mechanism, or, rather, the equation describing the decomposition, remains unchanged at different temperatures, the curves superimpose, showing that, for any value of t_r at the temperatures T_1, $T_2, \ldots T_n$, the values of α are the same.

The results of these calculations are presented in Fig. 2. These results show that particular curves can be described by one function dependent on the mechanism of the reaction. It is, therefore, possible to determine the value of the apparent activation energy E from the equation:

$$\log t_{1/2} = \log \frac{\text{constant}}{A} + \frac{E}{RT} \tag{5}$$

The slope of the plot of $\log t_{1/2}$ versus $1/T$ will yield the value of E. Such a plot is shown in Fig. 3. The value of the activation energy calculated from these experiments is 18 500 cal mol^{-1}. Isothermal measurements may

TABLE 1

Temperature in K, percentage weight loss after the completion of the reaction, time taken to reach $\alpha = 0.5$ and percentage of P in the product of the first step of thermal decomposition of diammonium hydrophosphate

Temperature (K)	Weight loss (%)	$t_{1/2}$ (h)	P content in product (%)
333	12.97	457	26.65
353	13.01	98	26.75
373	12.95	22.5	26.86
383	12.84	12.1	26.73
393	12.94	6.1	26.89
403	12.93	3.8	26.68
408	12.99	2.6	26.93
413 (6 h)	13.02	1.95	–
413 (60 h)	13.15	–	Product melted
413 (200 h)	13.40	–	Product melted
423	–	1.05	Product melted

TABLE 2

The reaction progress α as a function of time for the first stage of the thermal decomposition of diammonium hydrophosphate taken at temperatures of 353, 383 and 408 K (t_r = reduced time)

353 K			383 K			408 K		
t (h)	α	t_r	t (h)	α	t_r	t (h)	α	t_r
24	0.1576	0.2449	3	0.1590	0.2479	1	0.2104	0.3851
48	0.2736	0.4898	6	0.2840	0.4959	2	0.3955	0.7695
72	0.3878	0.7347	9	0.4012	0.7438	3	0.5545	1.1543
96	0.4873	0.9796	11	0.4707	0.9091	4	0.6868	1.5398
168	0.8317	1.7143	14	0.5618	1.1570	5	0.7924	1.9234
192	0.9101	1.9592	17	0.6477	1.4050	6	0.8698	2.3081
216	0.9193	2.2041	20	0.7228	1.6529	7	0.9234	2.6923
240	0.9785	2.4490	24	0.8026	1.9835	8	0.9543	3.0772
264	0.9977	2.6939	27	0.8507	2.2314	9	0.9711	3.4624
336	0.9986	3.4286	30	0.8886	2.4793	10	0.9803	3.8461
			33	0.9192	2.7273	11	0.9880	4.2314
			36	0.9410	2.9752	12	0.9916	4.6153
			40	0.9653	3.3058			
			43	0.9778	3.5537			

make it possible to choose the form of the $g(\alpha)$ function describing the mechanism of the decomposition. The comparison of the curves plotted in the co-ordinate system $\alpha-t_r$ with "master curves" [19,20] plotted for the functions based on various assumptions concerning the reaction rate-limiting stage allows us to choose the equation that best describes the course of the process. A similar method is the so called "ln–ln method" based on the Avrami–Erofeev equation,
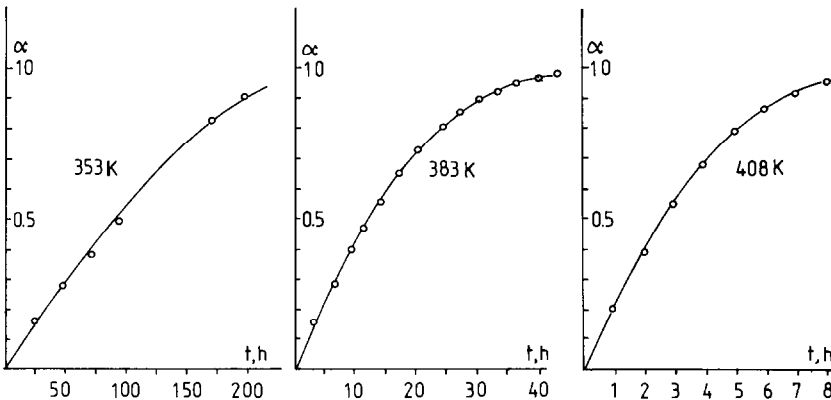
$$1 - \alpha = \exp(-kt)^n \tag{6}$$

Fig. 1. Fraction decomposed: α as a function of time for the first step of the isothermal decomposition of diammonium hydrophosphate at 353, 383 and 408 K.
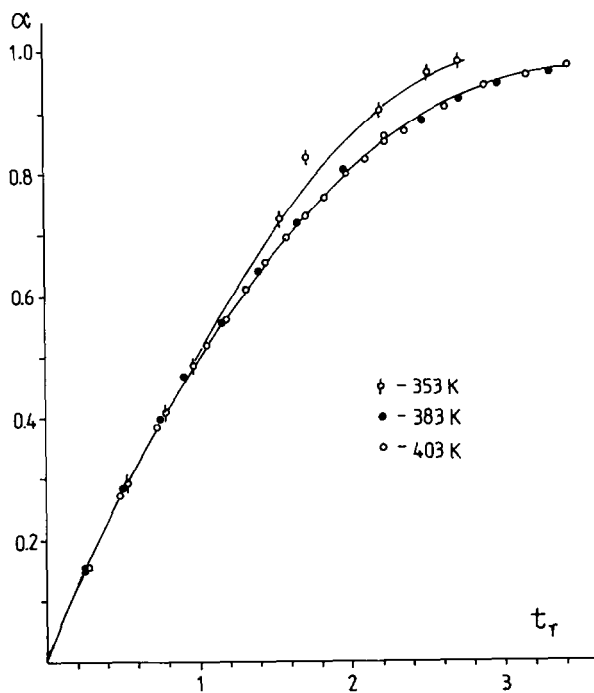
Fig. 2. Fraction decomposed: α versus reduced time t_r at temperatures of 353, 383 and 403 K.
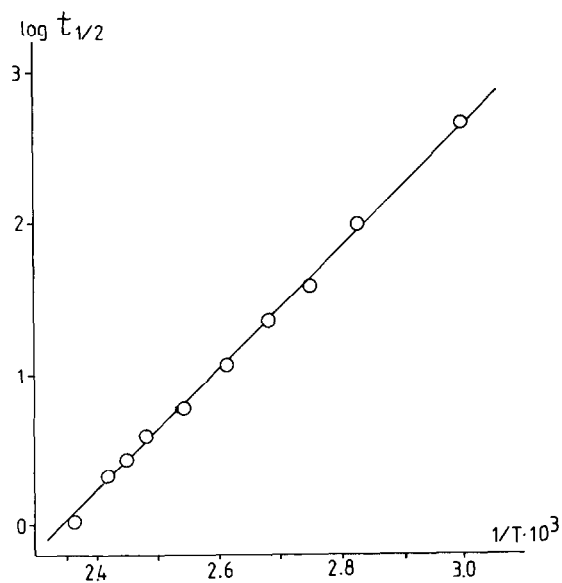

Fig. 3. Plot of $\log t_{1/2}$ versus $1/T$ for the first step of diammonium hydrophosphate decomposition.

which can be transformed to the form:

$$\ln(-\ln(1-\alpha)) = n \ln t + \text{constant} \tag{7}$$

The diagram in the system $\ln(-\ln(1-\alpha))$ versus $\ln t$ allows us to choose the form of the $g(\alpha)$ function, since the slope of the straight line is dependent on the function form. The values of n were calculated for kinetic expressions, e.g. the values of n for diffusion-limited equations are in the 0.54–0.62 range, for phase boundary controlled reactions, in the 1.07–1.11 range and for the Avrami–Erofeev equation they are 2.00 and 3.00.

The diagrams made in the discussed co-ordinate system and the comparison of the data with "master curves" showed that the $R2$ and $R3$ equations (for the symbols of the equations see nomenclature in [16]) describe the experimental data best, which indicates that the thermal decomposition can be regarded as a phase boundary controlled reaction. The choice of these equations may provide some information about the possible reaction mechanism, but, as such, it is, of course, no evidence for the real course of the process, and, apart from that, the choice of a particular equation on the basis of the procedure discussed above is in certain cases very difficult.

Method 2. The method of the determination of kinetic parameters was based on work published previously [21] by one of the authors of the present paper. This work dealt with the method of selection of a function describing the thermal decomposition of solids, that is, the selection of a relationship between α and t described by the equation

$$g(\alpha) = kt \tag{8}$$

(where k is the rate coefficient) in order to obtain the best fit to the experimental data.

The list of 16 kinetic functions and the method of their selection is given in [21]. The calculations, realized using a program written in Basic for 48k microcomputer, showed that the best fit to the experimental results is also given by equations $R2$ and $R3$, i.e. $1-(1-\alpha)^{1/2}$ and $1-(1-\alpha)^{1/3} = kt$, respectively.

Examples of calculations for the temperature of 373 K are given in Table 3, where r is the correlation coefficient and

$$R = \frac{1}{n} \sum_{i=1}^{n} (\alpha_{\text{calc},i} - \alpha_{\text{exp},i})^2 \tag{9}$$

n is the number of experimental values, $\alpha_{\text{exp},i}$ is the fraction decomposed for a given time t, and $\alpha_{\text{calc},i}$ is the α value calculated for a given time t on the basis of the corresponding $g(\alpha)$ function that equals kt.

The values of A and E for all the forms of the $g(\alpha)$ function used for the calculations are listed in Table 4.

According to the method of selection of the $g(\alpha)$ function, different values of the kinetic parameters for A and E can be obtained (see [21] and

TABLE 3

Results of the calculations of the criteria for the selection of g(α): $T = 373$ K, unweighted least-squares method. For the meaning of R see text

g(α)	Correlation coefficient	R
α^2	0.9905	0.00468
$\alpha^{1/2}$	0.9367	0.04179
$\alpha^{1/3}$	0.9157	0.07656
$\alpha^{1/4}$	0.9040	0.09775
$1-(1-\alpha)^{1/2}$	0.9992	0.00037
$1-(1-\alpha)^{1/3}$	0.9964	0.00083
$-\ln(1-\alpha)$	0.9645	0.00760
$-\ln(1-\alpha)^{2/3}$	0.9943	0.00192
$-\ln(1-\alpha)^{1/2}$	0.9980	0.00878
$-\ln(1-\alpha)^{1/3}$	0.9911	0.03240
$-\ln(1-\alpha)^{1/4}$	0.9831	0.05457
$(1-\alpha)\ln(1-\alpha)+\alpha$	0.9793	0.01231
$(1-2\alpha/3)-(1-\alpha)^{2/3}$	0.9672	0.01781
$[1-(1-\alpha)^{1/3}]^2$	0.9269	0.03311
$\ln \alpha/(1-\alpha)$	0.9863	0.06963
$1/(1-\alpha)-1$	0.7296	0.09675

[22]). In the case of the first stage of the thermal decomposition of DAHP investigated by the authors of this paper, the values of A and E are very close for the different forms of g(α), which makes the selection of the

TABLE 4

Values of the activation energy E (cal mol^{-1}) and pre-exponential factor A (min^{-1}) for the first step of diammonium hydrophosphate decomposition for different g(α) functions

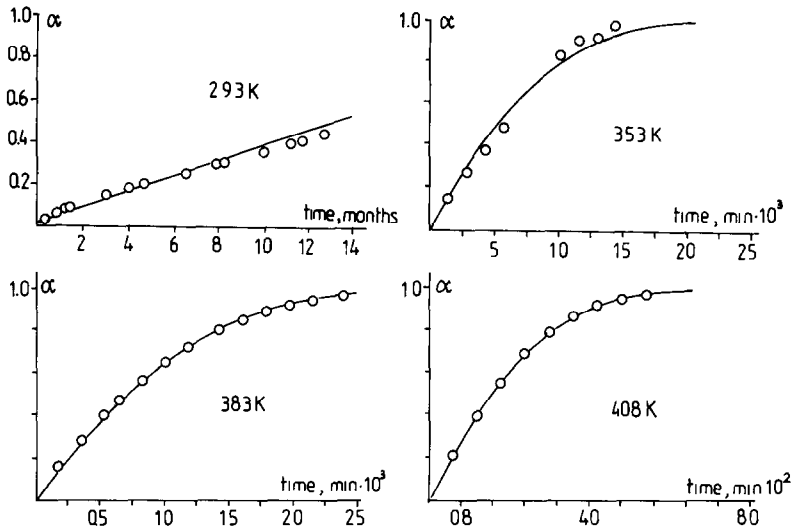| g(α)	E	A ($\times 10^7$)
α^2	18242	1.003
$\alpha^{1/2}$	18407	1.423
$\alpha^{1/3}$	18317	1.238
$\alpha^{1/4}$	18272	1.112
$1-(1-\alpha)^{1/2}$	18445	1.504
$1-(1-\alpha)^{1/3}$	18605	1.335
$-\ln(1-\alpha)$	18101	2.907
$-\ln(1-\alpha)^{2/3}$	18421	3.315
$-\ln(1-\alpha)^{1/2}$	18480	3.130
$-\ln(1-\alpha)^{1/3}$	18302	1.826
$-\ln(1-\alpha)^{1/4}$	18259	1.519
$(1-\alpha)\ln(1-\alpha)+\alpha$	18230	0.880
$(1-2\alpha/3)-(1-\alpha)^{2/3}$	18184	0.237
$[1-(1-\alpha)^{1/3}]^2$	18037	0.337
$\ln/(1-\alpha)$	18337	3.713
$1/(1-\alpha)-1$	16711	3.253

Fig. 4. $\alpha-t$ relationships at 293, 353, 383 and 408 K, calculated on the basis of the following kinetic parameters: $E = 18\,300$ cal mol^{-1}, $A = 8.0 \times 10^6$ min^{-1}, $g(\alpha) = 1 - (1 - \alpha)^{1/3}$. Experimental results are marked on the curves as circles.

function even more difficult. This fact supports the above remarks: the attributing of a physical meaning to definite values of $g(\alpha)$ should be done with considerable caution.

The choice of a given form of $g(\alpha)$ does not provide information on the reaction mechanism, on the basis of which this function was derived theoretically: it only means that the given function, in comparison with other expressions used for calculations, best describes mathematically the experimental results. The applicability of the kinetic parameters A, E and $g(\alpha)$ in the studies of the reaction mechanism is rather doubtful, and these expressions, if treated as mathematical parameters only, may be very useful for the correlation of the results obtained in isothermal and dynamic conditions, or for the prediction of the $\alpha-t$ relationship at temperatures that are different from the ones used experimentally.

Figure 4 presents the $\alpha-t$ relationship calculated on the basis of the kinetic parameters for the temperatures of (a) 20, (b) 80, (c) 100 and (d) 135°C, respectively. The following data were taken for the calculations: $E = 18\,300$ cal mol^{-1}, $A = 8.0 \times 10^6$ min^{-1}, $g(\alpha) = 1 - (1 - \alpha)^{1/3}$.

(B) Rising temperature experiments

During the heating of DAHP, depending on the heating rate, the product of the first stage of the thermal decomposition $(NH_4H_2PO_4)$ starts to decompose within a temperature range of 180–190°C. Simultaneously, in this range of temperatures, a liquid phase occurs in the system (the melting
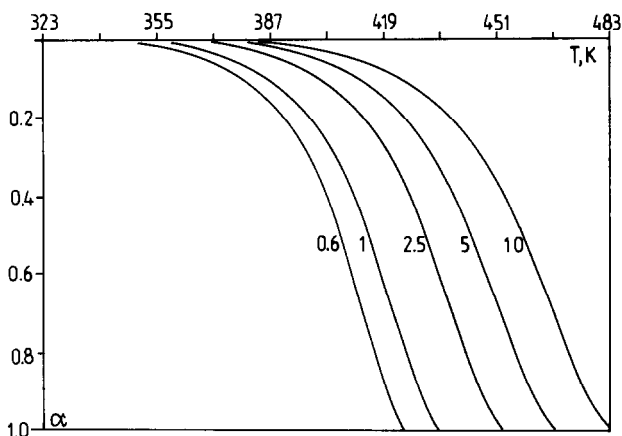
Fig. 5. Theoretically calculated $\alpha - T$ relationships for the following kinetic parameters: $E = 18\,500$ cal mol^{-1}, $A = 1.0 \times 10^7$, $g(\alpha) = 1 - (1 - \alpha)^{1/3}$, heating rates of 0.6, 1, 2.5, 5 and 10 K min^{-1}.

of $NH_4H_2PO_4$ is observed). Both phenomena superimpose, thus complicating the first stage of the decomposition of DAHP, if the process, in dynamic conditions, is not completed before the temperature reaches $180\,°C$.

The kinetic parameters calculated from isothermal measurements enable the theoretical determination of the $\alpha - T$ relationship at different heating rates ([23] and refs. therein). The results of the calculations for the values of $E = 18\,500$ cal mol^{-1}, $A = 1.0 \times 10^7$ min^{-1} and $g(\alpha) = 1 - (1 - \alpha)^{1/3}$ are presented in Fig. 5. It is evident from this figure that the total decomposition ($\alpha = 1$) below $180\,°C$ may only be achieved if the heating rates are lower than $2.5\,°C$ min^{-1}. The application of higher heating rates will cause the shift of the end of the decomposition towards higher temperatures, and, therefore, additional physicochemical phenomena (melting and the decomposition of $NH_4H_2PO_4$) will affect the decomposition of DAHP.

The above calculations were confirmed by the measurements made at the heating rates of 1, 5 and $10\,°C$ min^{-1}. The results of the studies are shown in Fig. 6. At the heating rate of $1\,°C$ min^{-1} the value $\alpha = 1$ is reached at the temperature of $167\,°C$. DTA and TG curves indicate that the reaction proceeds in one stage, and that it is an endothermic process with the maximum at $153\,°C$. At the heating rate of $5\,°C$ min^{-1}, the endothermic effect of the decomposition, whose maximum is at $170\,°C$, is superimposed by a distinct endothermic effect, which means that the liquid phase occurs in the system (initial temperature of the peak, $175\,°C$; maximum temperature, $181\,°C$). No horizontal part can be seen on the TG curve, only a distinct inflexion of the curve is observed, which means that the two stages superimpose (the end of the decomposition of $(NH_4)_2HPO_4$ and the beginning of the decomposition of $NH_4H_2PO_4$).
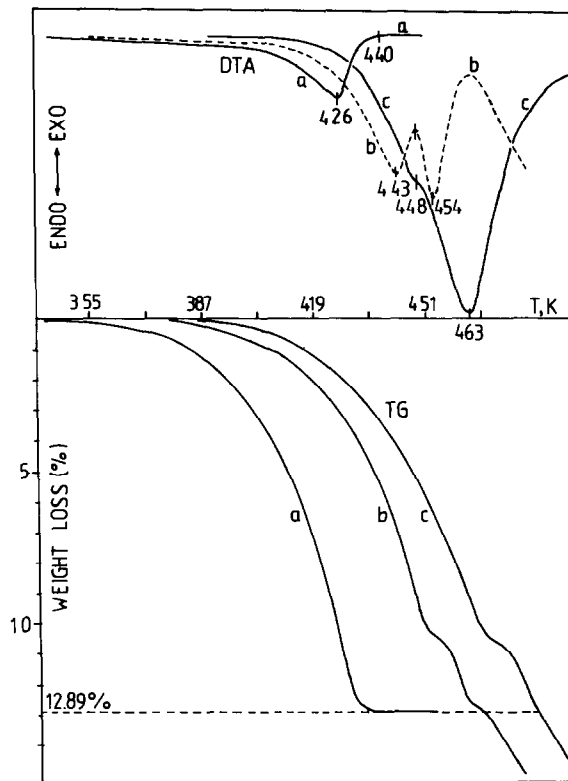
Fig. 6. Thermal decomposition of diammonium hydrophosphate at heating rates of (a) 1, (b) 5 and (c) 10 K min^{-1}. The sample mass was 46.8 mg, static air atmosphere. Theoretical weight loss for the first step of the decomposition, 12.89%, is marked on the figure.

The first stage of the decomposition is disturbed by the occurrence of the liquid phase in the system which causes a slight decrease in the reaction rate. This phenomenon is still more visible at the heating rate of 10°C min^{-1}. At the temperature of 175°C begins the distinct endothermic effect of melting (maximum at 192°C, the value of the fraction decomposed $\alpha = 0.45$), whereas, at the temperature of 200°C, a noticeable inflexion at the value of $\alpha = 0.86$ occurs on the TG curve. Above this temperature, the decomposition of $NH_4H_2PO_4$ proceeds at an increasing rate, but no inflexion, indicating the end of the first stage of the decomposition of DAHP, can be observed on the curve.

In Fig. 7 the experimental and calculated data are compared on the basis of the knowledge of the kinetic parameters. It can be clearly seen how additional physicochemical phenomena (melting and the beginning of the decomposition of the product of the first stage) affect the decomposition process, and how the comparison of the experimental and theoretical curves facilitates the interpretation of the results of the thermal analysis.
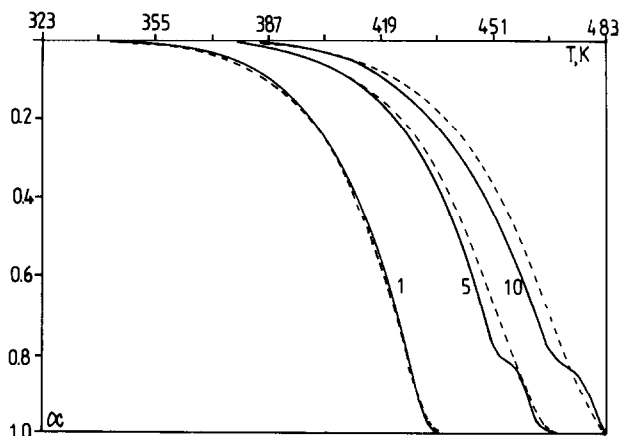
Fig. 7. Thermal decomposition of diammonium hydrophosphate at heating rates of 1, 5 and 10 K min^{-1}. The values of Φ are marked on the curves. Dashed lines represent theoretical $\alpha-T$ relationships for particular values of Φ calculated using kinetic parameters identical with those in Fig. 5.

The results of the studies of the decomposition of DAHP show how risky it is to draw conclusions, on the basis of non-isothermal results, if the conclusions are not supported by the results of kinetic studies. To illustrate the problem better, theoretical results of calculations are given below for the thermal decomposition process characterized by the parameters $E = 20\,000$ cal mol^{-1}, $g(\alpha) = 1 - (1 - \alpha)^{1/3}$ and values of A varying from 1×10^7 to 1×10^{10} min^{-1}.

Calculations were made for the heating rate of 5°C min^{-1}. The $\alpha-T$ relationships calculated for these conditions are presented in Fig. 8. The curve for the value $A = 1 \times 10^9$ min^{-1}, chosen for further considerations, shows that, in the measurement conditions applied, the initial temperature of the decomposition determined from the TG curve was about 85°C.

For identical values of A, E and $g(\alpha)$, but at a heating rate of 10°C min^{-1}, the initial temperature of the decomposition, determined on the basis of the TG curve, was 95°C, and at $\Phi = 1$°C min^{-1}, 70°C. At the heating rate of $\phi = 5$°C min^{-1} a temperature of 85°C would be regarded as the temperature below which a compound is thermally stable. Calculations made using identical kinetic parameters, but in isothermal conditions show, however, that at the temperature of 90°C (after about 1000 min) the compound could undergo total decomposition. The $\alpha-t$ relationship for the temperatures of 60, 70, 80 and 90°C is shown in Fig. 9. Even at the temperature of 60°C, after 1000 min, the degree of the decomposition is about 0.2.

The above theoretical considerations well illustrate the results of the studies of DAHP presented in this paper. The literature values of "the initial
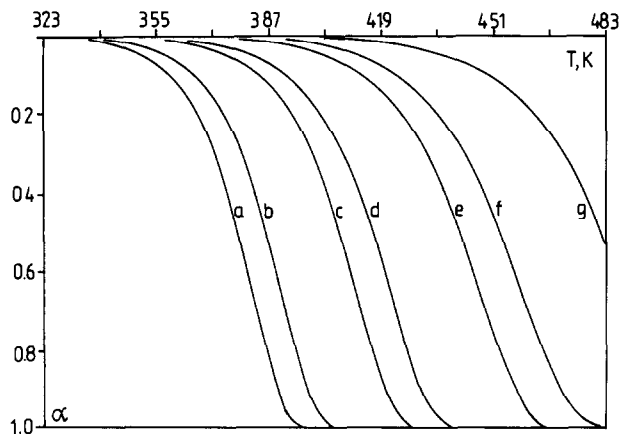
Fig. 8. Theoretical $\alpha - T$ relationships for the thermal decomposition process with the kinetic parameters: $E = 20\,000$ cal mol^{-1}, $g(\alpha) = 1 - (1 - \alpha)^{1/3}$, heating rate 5 K min^{-1}, $A = $ (a) 1×10^{10}, (b) 5×10^{9}, (c) 1×10^{9}, (d) 5×10^{8}, (e) 1×10^{8}, (f) 5×10^{7}, (g) 1×10^{7} min^{-1}.

temperature of decomposition", or the temperatures at which a compound can be dried safely without undergoing decomposition, determined on the basis of dynamic measurements in different measurement conditions, give, practically, no relevant information about the behaviour of a given compound in isothermal conditions. For example, $(NH_4)_2HPO_4$, whose "initial temperature of decomposition" is defined in the literature on the basis of rising temperature experiments as over 100°C [1–5,8] after 24 h drying at the temperature of 80°C exhibits a total percentage weight loss of 15%.
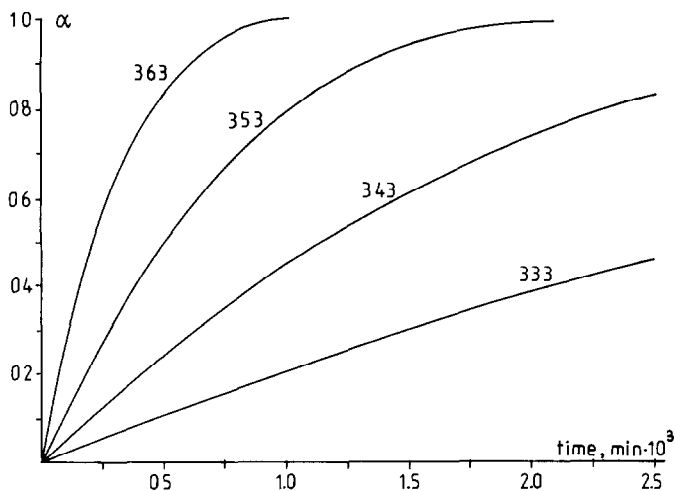

Fig. 9. Theoretical $\alpha - t$ relationships for the isothermal decomposition process ($E = 20\,000$ cal mol^{-1}, $g(\alpha) = 1 - (1 - \alpha)^{1/3}$, $A = 1 \times 10^{9}$ min^{-1}). Temperatures (in K) are marked on the curves.

CONCLUSIONS

The product of the first stage of the thermal decomposition of DAHP is $NH_4H_2PO_4$, which was confirmed by the results of thermal analysis, quantitative chemical analysis, X-ray powder analysis and by chromatography. Below a temperature of 150°C, in isothermal measurements, it is possible to stop the reaction after the first stage: at higher temperatures, before the completion of the first stage, the decomposition of $NH_4H_2PO_4$ begins, and the liquid phase occurs in the system. The last two phenomena affect the course of the first stage, which can be seen particularly in non-isothermal measurements. If a fast heating rate is applied to the system (10 or even 5°C min^{-1}), additional effects occur on DTA–TG curves during the decomposition of DAHP. At a slow heating rate (1°C min^{-1}), in the measurement conditions used in the present work, the process of the thermal decomposition of DAHP runs according to the equation

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3 \qquad (10)$$
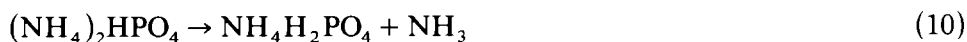
in one stage, and the total evolution of 1 mol of ammonia takes place below 170°C.

The kinetic parameters (the g(α) function, A and E) determined on the basis of isothermal measurements enabled the determination of TG curves in rising temperature conditions. Theoretical calculations were confirmed by experimental results.

The comparison of theoretical and experimental curves of thermal analysis enables a more accurate interpretation of the results obtained in dynamic conditions. The differences between these curves may help to highlight additional physicochemical phenomena taking place in the course of the thermal decomposition, such as the occurrence of the liquid phase in the system.

The theoretical curve included in the paper, and the results of the experiments, show that drawing conclusions concerning the stability of compounds on the basis of dynamic measurements carried out at high heating rates may certainly be misleading. Assuming, for a given compound, the stability of the mechanism of the decomposition in a wide range of temperatures, i.e. the invariance of the form of the g(α) function, the beginning of the decomposition observed on TG or DTA curves is dependent on the heating rate, if the values A and E are constant in experimental conditions. In the case of compounds having small activation energies, about 20 000 cal mol^{-1}, the initial temperature of the decomposition, determined from the curves which were obtained in dynamic conditions, will oscillate within a 90–100°C range at normally applied heating rates of 5°C min^{-1}. Accepting these temperatures as the values below which a compound is stable may be the source of significant errors. It should be noted that the compound heated isothermally, even at a temperature lower by 40–50°C

than "the initial temperature of decomposition", may exhibit a considerable degree of decomposition after several hours. The knowledge of the kinetic parameters may in this case facilitate the carrying out of the correlation between isothermal and dynamic measurements, provided that these parameters are stable, regardless of the experimental conditions.

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