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Study of the decomposition of phase stabilized ammonium nitrate (PSAN) by simultaneous thermal analysis: determination of kinetic parameters

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Abstract

Ammonium nitrate (AN) has been extensively used both in explosive and propellant formulations. Unlike AN, there is a lack of information about the thermal decomposition and related kinetic analysis of phase stabilized ammonium nitrate (PSAN). Simultaneous thermal analysis (DSC-TG) has been used in the thermal characterisation of a specific type of PSAN containing 1.0% of NiO (stabilizing agent) and 0.5% of Petro (anti-caking agent) as additives. Repeated runs covering the nominal heating rates range from 2.5 to 20 K min^{-1} allowed to conclude on the good reproducibility of the main features of the thermal behavior of PSAN, i.e., two phase transitions, melting and decomposition. Non-isothermal kinetic analysis has been used to estimated the Arrhenius parameters of the decomposition process by applying both a single curve method and two isoconversion methods to the TG data. The results are discussed considering the range of applicability of the methods as well as the influence of the experimental conditions and/or techniques in the kinetic analysis results in a broader sense. A systematic approach based on the isoconversion methods results and statistical tools has been adopted to obtain reliable estimates of the Arrhenius parameters for the thermal decomposition of PSAN. Under the condition of study, the values of 81.4 ± 3.5 kJ mol^{-1} for the activation energy and $(5.63\pm0.01)\times10^5$ s^{-1} for the pre-exponential factor were found as describing the process over a wide range of the kinetic analysis. © 1998 Elsevier Science B.V.

Keywords: Ammonium nitrate (AN); Phase stabilized ammonium nitrate (PSAN); Kinetic parameters; Simultaneous thermal analysis; Thermal decomposition

1. Introduction

Ammonium nitrate (AN) is a well-known oxidizer used for many years both in explosive and propellant formulations. Some reasons for this are its low cost, chemical stability, low sensitivity to friction and to shock, as well as its low polluting characteristics. Its use as a main propellant ingredient has been somewhat limited due to its high hygroscopicity, solid state phase transition characteristics, particle shape, low energy and low reactivity. Despite these drawbacks the AN has gained a new interest in the last years, namely because efforts are being made to overcome the environmental problems posed by the propellants based on ammonium perclorate (AP). In the view of the costs that would be involved in the search for new oxidizers the possible replacement of AP by AN for

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some applications is still a matter of interest [1–7]. To reduce its low performance characteristics, AN has been formulated with reactive metals [5] as well as with energetic binders [1,2]. Furthermore, efforts have been made in developing different kinds of phase stabilized ammonium nitrate (PSAN) [8,9] to minimize the undesirable physical properties, and its effects, characterizing ordinary AN.

It has been reported [8,10] that at least five different polymorphic forms for AN exist at atmospheric pressure, being the correspondent transition temperatures as follows:

$$\mathrm{AN_V} \overset{255\,\mathrm{K}}{\rightarrow} \mathrm{AN_{IV}} \overset{305\sim328\,\mathrm{K}}{\rightarrow} \mathrm{AN_{III}}$$

$$\overset{357\,\mathrm{K}}{\rightarrow} \mathrm{AN_{II}} \overset{398\,\mathrm{K}}{\rightarrow} \mathrm{AN_I} \overset{443\,\mathrm{K}}{\rightarrow} \mathrm{melt}$$

or

$$\cdots \mathrm{AN_{IV}} \overset{325\,\mathrm{K}}{\rightarrow} \mathrm{AN_{II}} \cdots$$

However, these figures for the transition temperatures are not always reproducible, not only between different samples but also within the same sample. The transition temperatures of AN are dependent on several factors as well as on its inter-relationships [8,10]. Several methods have been reported to produce either pure AN or different types of PSAN [8,11]. The low water content of these products permits the direct phase transition IV→II, thus avoiding the undesirable problems due to crystal volume changes occurring during the transition IV→III. Besides, small particle sizes with spherical shape can be obtained [11].

In parallel with its wide application in energetic formulations the thermal decomposition of AN has been studied extensively [12–22]. A great deal of work has been done on the kinetics and mechanisms of decomposition whose possible variety seems to strongly dependent on the experimental conditions such as the pressure, sample size, state of confinement, heating rate, and the presence of traces of impurities or additives [14]. This can explain to some extent the surprisingly wide range of activation energy values reported for the thermal decomposition of AN, ranging from 118 [15] to 171.5 kJ mol^{-1}[17]. These studies have been carried out under different experimental conditions, possibly by means of experimental setups specifically designed to reach a restricted goal.

With the advent of thermoanalytical commercial apparatus (DSC, DTA, TGA), the kinetic analysis based on thermoanalytical data became popular. It was made possible to establish a uniform technique applied to thermal analysis studies, which does not necessarily mean that a desirable reproducibility of results have been attained. Analyzing the influence of the sample size in the kinetic analysis based on thermoanalytical data, Koga and Tanaka [23,24] have chosen the thermal decomposition of AN as a suitable process for that study. They found values for the activation energy ranging from 83.8 to 97.9 KJ mol^{-1} depending on the sample mass and/or the temperature regime. There is a lack of information concerning the kinetic parameters of the thermal decomposition of PSAN. A value for the activation energy close to 113 KJ mol^{-1} by assuming a priori a first-order decomposition kinetic has been reported in a recent work [5], but it has been underlined that this figure was determined mainly for comparative purposes directed to the particular context of the work. Thus it is pertinent to estimate using a reliable procedure, the kinetic parameters characterizing the thermal decomposition of PSAN, not only in view of an original contribution circumscribed to a particular type of PSAN but also as a comparative study regarding other works in which different conditions and/or types of AN have been employed.

This work is a study of the thermal decomposition of a type of PSAN, which contains 1% of NiO and 0.5% of Petro (sodiumlaurylsulfonate) as additives, under non-isothermal conditions by means of simultaneous thermal analysis. The phase transitions and melting processes are qualitatively discussed in the light of information available on AN without any specific additives. The kinetic analysis of the decomposition process is made and discussed in terms of the problem of uniqueness with parameters from non-isothermal analysis, and a systematic approach by using two isoconversion methods as well as some statistical tools are applied to substantiate the reliability of the kinetic parameters that have been found.

2. Theory

The basic equation for the most common methods of kinetic data evaluation is the well-known expression for the rate of the process in which it is assumed that the temperature dependence $k(T)$ is given by the

Arrhenius expression,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

where α is the degree of conversion, E the activation energy, A the pre-exponential factor, T the absolute temperature, R the gas constant, t the time, and $f(\alpha)$ the conversion model function. Assuming that A and E are independent of both T and α, and $f(\alpha)$ is independent of T, Eq. (1) can be integrated for the non-isothermal conditions' case (linear heating rate β) leading to

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \left(\frac{AE}{R\beta}\right)p(x)\left(x = -\frac{E}{RT}\right) \tag{2}$$

where $g(\alpha)$ is the integrated conversion function and $p(x)$ is a function that includes the exponential-integral for which either series expressions or semiempirical approximations have been proposed [25,26].

It is not unusual to find reported Arrhenius parameter values based on the Coats and Redfern [27] method in which the conversion model function is imposed a priori as $f(\alpha)=(1-\alpha)$, that is a first-order kinetic. According to this simplification and by applying logarithms to Eq. (2) after considering an asymptotic expression for $p(x)$ results

$$\ln\left[\ln\left(\frac{1-\alpha}{T^2}\right)\right] \simeq \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{3}$$

Past experience have demonstrated the weakness of such simplification in particular and of the single curve methods in general. Furthermore, these methods do not permit to check if the assumptions in which they are based are or are not violated.

To get around the problem of determining all kinetic parameters simultaneously, an isoconversion method should be used. This permits to estimate a more reliable value of E as well as to check the validity of the method itself. The isoconversion Ozawa–Flynn–Wall [28,29] is one of the most popular integral methods for estimating E by the linear relation

$$\log\beta + 0.4567\frac{E}{RT} \simeq \text{constant} \tag{4}$$

To avoid the assumption of linear heating rate and the approximation for $p(x)$ underlying Eq. (4), the method proposed by Friedman [30] can be used.

The expanded interpretation of this differential method has been presented by Ozawa [31,32]. The method is based on the logarithm form of Eq. (1)

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \tag{5}$$

Once a reliable value for E is obtained and its invariance with α and T checked, the value of A may be estimated provided that the form of $f(\alpha)$ is known. The useful concept of generalized time proposed by Ozawa [33] is expressed by

$$\theta = \int_0^t \exp\left(-\frac{E}{RT}\right)\mathrm{d}t \tag{6}$$

which by differentiation gives

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \exp\left(-\frac{E}{RT}\right) \tag{7}$$

Combining Eq. (1) and Eq. (7) results

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\theta} = Af(\alpha) \tag{8}$$

or

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}\theta}\frac{\mathrm{d}\theta}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}\theta}\exp\left(-\frac{E}{RT}\right) \tag{9}$$

Thus the kinetics may be described by dividing the rate of process into the enthalpy-dependent term, $\mathrm{d}\theta/\mathrm{d}t$, and the entropy-dependent term, $\mathrm{d}\alpha/\mathrm{d}\theta$ [24,34]. If a reliable value of E is known it is possible to determine the entropy-dependent term at different values of α and thus to evaluate both the value of A and the form of $f(\alpha)$ according to Eq. (8).

Unlike isothermal studies, the non-isothermal techniques permit to characterize the beginning of a thermal decomposition process in a more precise way. Flynn and Wall [28] have pointed out the usefulness of the initial values of the Arrhenius parameters in determining the overall mechanism. The E value can be estimated from initial rates without knowing the form of $f(\alpha)$ since all well-behaved reactions are nearly zero order for $\alpha\rightarrow 0$. By plotting $-\mathrm{d}\alpha/\mathrm{d}(1/T)(-T^2(\mathrm{d}\alpha/\mathrm{d}T)$ against α, the slope is given by $E/R + 2\bar{T}$ for low values of α, where $\bar{T}$ is the average temperature over the interval where the slope is determined, and $E/R \gg 2\bar{T}$ [28].

3. Experimental

3.1. Sample preparation

The PSAN used in this study was obtained from ICT, Germany. It contained 1.0% NiO, as phase stabilizing agent and 0.5% Petro (sodiumlaurylsulfonate), as anti-caking agent. The measured values for density and particle median diameter (d_{50}) were 1716 kg m^{-3} and 140 μm, respectively. Great care was taken to avoid the contact of the sample with moisture during transportation. The temperature and relative humidity in the room where the experiments were carried out were maintained within the limits of 20–27°C and 20–25%, respectively.

3.2. Thermal analysis instruments, conditions and procedures

Simultaneous thermal analysis (heat flux DSC and TGA) was employed to investigate the thermal decomposition of PSAN in non-isothermal conditions. The measurements were carried out using a *Rheometric Scientific* STA 1500 equipment. Temperature calibrating for both modules (DSC and TGA) were performed in the range 298–773 K by running melting standards such as Indium, Tin and Lead (purity: 99.999%, according to the equipment manufacturer). The same standards were used in order to obtain calorimetric results in the DSC module. These calibrations were performed for each heating rate (2.5, 5, 10, 15 and 20 K min^{-1}) used in the subsequent experiments. The heating rates have been checked by running empty crucibles; the actual values of 2.5, 5.1, 10.3, 16 and 21.8 k min^{-1} have been employed in all calculations performed. The gain of the thermobalance was chosen to give an approximate resolution of 0.3 μg. The samples were loaded into open alumina crucibles and a dry nitrogen purge flow of 50 ml min^{-1} at 0.1 MPa absolute pressure was used in all measurements.

The experimental procedure was planned to give, as much as possible, relevant information for the subsequent data treatment and to evaluate the reliability of dependencies between variables from a statistical point of view. Four measurements were performed for each heating rate by using a sample size of 2.13±0.05 mg. This allows to account for both the instrumental and process factors in the calculation of the kinetic parameters and thus to obtain an acceptable figure for the respective uncertainties.

4. Results and discussion

4.1. Thermal decomposition of PSAN

Fig. 1 shows typical DSC and TG curves for PSAN over the temperature range within which the thermal

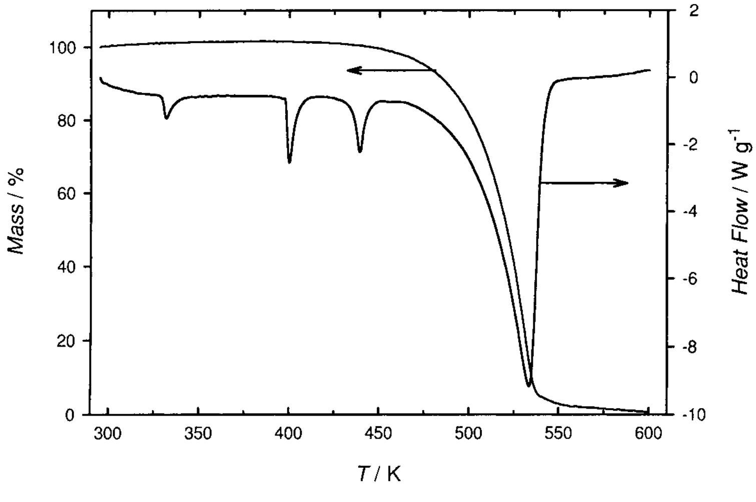

Fig. 1. Typical TG and DSC curves for PSAN.

Table 1
Endothermic peak temperatures (K) for PSAN

β (K min^{-1})	Transformation			
	IV→II	II→I	I→Melt	Decomposition
2.5	330.1±0.1	398.3±0.1	437.0±1.4	497.0±1.7
5	330.5±0.4	398.7±0.3	438.4±0.9	515.5±2.3
10	331.6±0.3	399.4±1.9	439.2±0.4	533.7±0.7
15	332.0±0.4	400.1±0.4	439.6±0.2	545.5±0.9
20	332.3±0.3	400.6±0.5	439.6±0.3	551.6±1.4

events occur, obtained at a heating rate of 10 K min^{-1}. From the DSC curve it is possible to identify two first endothermic peaks near 332 and 398 K due to phase transitions IV→II and II→I, respectively. As expected, for PSAN the transition between the phase IV and III is absent. The endothermic peak corresponding to the melting occurs near 439 K, after which the decomposition starts and the respective peak is reached at approximately 531 K. The TG curve also shows that the decomposition occurring after the melting ends is the cause of the main mass loss. However, some reactive process may start even during the melting process. A slight mass loss has been detected before the melting was completed. The DSC/TG curves obtained by employing the heating rates 2.5, 5, 15 and 20 K min^{-1} are qualitatively similar to the curves presented in Fig. 1.

Table 1 presents the mean values with error of the peak temperatures. A remarkable repeatability has been obtained in most of the runs carried out at each heating rate, mainly in what concerns to the phase transition and melting temperatures. Although a larger dispersion has been encountered in the peak temperatures corresponding to the decomposition, it was within acceptable levels taking into account the thermochemical character of such a process. Even when the controlled measuring conditions (heating rate, sample mass, purge gas flow rate) are maintained approximately constant from run to run, the self-generated reaction conditions characterizing the decomposition are not controlled in a strict sense. Thus small differences in the overall process between runs may explain some variability.

It was not found in the literature any systematic thermal study on experimental factors affecting the phase transitions of PSAN, while, for AN, some studies have been reported [10,35]. It is generally accepted that the transition temperatures are dependent on several factors as well as on its inter-relationships [8,10]. The best known of these factors are the water content, impurity content, and the thermal history, but others more difficult to identify or even quantify exist [10]. The water content is recognized to be responsible for the phase transition IV→III as well as for the wide temperature range within which this transition can occur. The overall consistence of the results of the present work substantiates the reliability of the transition temperatures of the particular type of PSAN used, under the conditions of study.

4.2. Determination of kinetic parameters

4.2.1. Considerations on data treatment and calculation procedures

The kinetic analysis of the thermal decomposition of PSAN has been based on the TG curves. There are several possible sources of errors in kinetic analysis based on thermoanalytical data, arising from the experimental measurements to the mathematical modeling of the process under study. Thus the quantification of the uncertainty of the result is strongly recommended. Accordingly, instead of choosing the best set of experimental data that would lead to higher correlation coefficients in the regression procedures, all runs have been included when fitting data to the models for estimating the Arrhenius parameters. All the uncertainties presented are based on a 95% confidence level.

In a strictly mathematical sense, checking the adequacy of each (linear) model employed is also an imperative procedure for reliable results of the parameters. The regression coefficient is an index of fit commonly used, but a high value for this coefficient can be deceptive. Hidden anomalies in the data structure may exist, that when ignored can result in biased regression parameters (thus, in Arrhenius parameters whose values appear to be distorted due to purely mathematical inadequacies). Therefore, other statistical tests than the simple evaluation of the regression coefficient, such as a careful residual analysis, are strongly recommended. This permits to check the model in what concerns to the assumptions that are inherent to the linear least squares (normal distributed independent errors with zero mean, and a constant variance [36]). For detecting possible anomalies (that can result in biased regression coefficients) the most common plots are: the residuals against the predicted values; the residuals against the predictor variable; and the expected normal values against the residuals [36]. All these tests have been performed for each regression. Furthermore, the possible existence of outliers (an atypical observation that may have a strong influence on the regression line and thus in the regression parameters) has been checked by searching for cases falling outside the interval defined by ±2 times the standard deviation of the residuals. Whenever outliers have been found the correspondent cases have been examined in detail. This allowed to conclude that the regression coefficients were not significantly affected by the exclusion of the outliers. Since some extreme experimental points may be highly significant and suggestive in the sense that they can reflect some physico-chemical factor intrinsic to the process under study rather than an experimental error, it has been decided to choose the results in which the outliers have been included despite the higher uncertainties associated to the Arrhenius parameters thus obtained.

4.3. Single curve method

It has been reported in several works on the thermal decomposition of AN [18,19,21,22] that the overall decomposition process was described by a first-order kinetics under the studied conditions. However, the rate law of a reaction is determined experimentally, and thus the Arrhenius parameters as well as the reaction order have a purely empirical meaning. Experimental conditions play an important rule in the solid decomposition processes and therefore in the respective kinetic analysis results. This can explain the lack of reproducibility of results of measurements, namely in the Arrhenius parameters values.

In order to show in practical terms, the already mentioned pitfalls concerning the determination of kinetic parameters by a single thermoanalytical curve, the Coast and Redfern [27] method has been applied to our experimental data considering a priori a first-order kinetics, that is $f(\alpha)=(1-\alpha)$. Furthermore, it is intended to show how the usual criterion for linearity based only on a high regression coefficient can lead to erroneous results. Eq. (3) has been applied to the experimental results obtained for the heating rate of 10 K min^{-1}, and several ranges of α have been used for the calculation of the Arrhenius parameters. The results are summarized in Table 2. It can be observed that whatever the range of α considered, good correlation coefficients are obtained. However, E, and consequently A due to the mutual dependence, exhibit a considerable variation within the range of α used. The question to be raised is to know what would be the correct result. For example, the value of 113.7±3.7 kJ mol^{-1} is approximate to the values reported in other works [5,15]. However, the reproducibility of this result does not necessarily warrants its reliability.

Table 2
Estimates of the Arrhenius parameters based on Coats–Redfern method

Range of α	E (kJ mol^{-1})	$\log(A/\mathrm{s}^{-1})$	r^{a}
0.05–0.75	109.0±3.1	8.8±0.1	0.9944
0.05–0.70	107.1±2.8	8.6±0.1	0.9954
0.05–0.65	105.4±2.6	8.4±0.1	0.9961
0.05–0.60	103.9±2.5	8.2±0.1	0.9967
0.05–0.55	102.4±2.4	8.1±0.1	0.9970
0.05–0.50	101.2±2.4	7.9±0.1	0.9974
0.05–0.45	100.0±2.4	7.8±0.1	0.9976
0.10–0.75	113.7±3.7	9.3±0.2	0.9931
0.10–0.70	111.4±3.5	9.0±0.2	0.9940
0.10–0.65	109.2±3.3	8.8±0.1	0.9947
0.10–0.60	107.2±3.3	8.6±0.2	0.9952
0.10–0.55	105.4±3.3	8.4±0.2	0.9954
0.10–0.50	103.6±3.4	8.2±0.2	0.9955
0.10–0.45	102.0±3.7	8.0±0.2	0.9954

[a] Regression coefficient.

A careful analysis of the mathematical model used would be sufficient to reveal its inadequacy and thus the questionable reliability of the correspondent parameters. The residual analysis appears to be an important tool to check the applicability of the model. For the present purpose it is sufficient to analyze the plot of the residuals against the predicted values. This is shown in Fig. 2 (where the observed systematic pattern (U shape) is indicative that the model presents lack of terms (parameters). Ignoring this, the obtained Arrhenius parameters should be questionable, as will be confirmed in the following discussion.

4.4. Isoconversion methods

The Ozawa–Flynn–Wall [28,29] and the extended Friedman [30–32] methods have been used to estimate

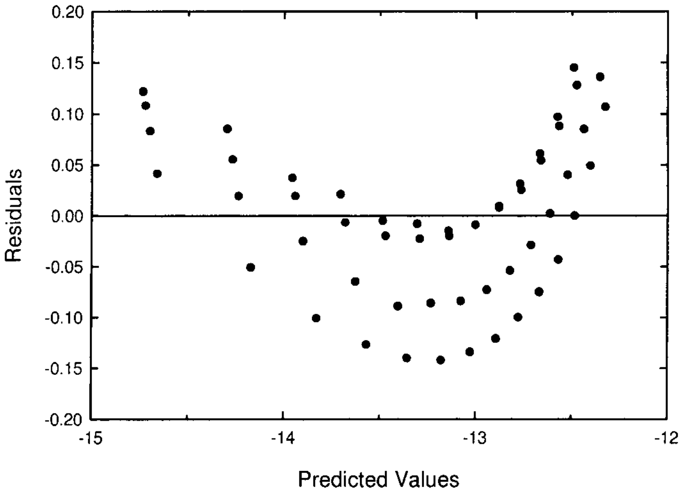

Fig. 2. Example of the residual analysis applied to Coasts–Redfern method. (The model is of the type $Y_i = B_0 + B_1X_i + \varepsilon_i$, where $\varepsilon_i = Y_i - \hat{Y}_i$ are the residuals and $\hat{Y}_i$ the predicted values.)

E independently of the choice of the function $f(\alpha)$, by applying Eq. (4) and Eq. (5) at different levels of α, ranging from 0.05 to 0.95 with a step size of $\Delta\alpha$=0.01. The results are depicted graphically in Fig. 3. The method of initial rates [28] has also been employed in the range of α from 0 to 0.1. A typical fitting to the experimental data is represented in Fig. 4 and the results obtained for each heating rate are also presented in Fig. 3. It seems clear that the early stage of the process is not influenced by the heating rate, as can be inferred from the nearly constant values of E over the range of heating rates studied. The value of E is also approximately constant over the range of α in which the isoconversion methods have been applied.

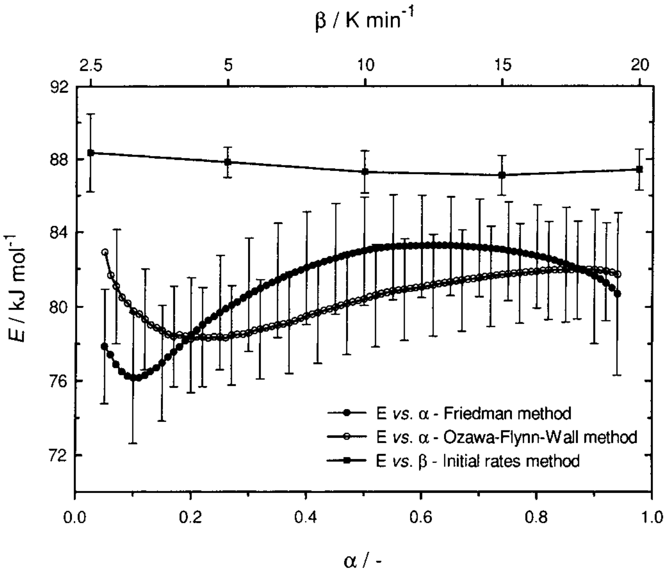

Fig. 3. Activation energy as a function of the degree of conversion (lower axis), and as a function of the heating rate (upper axis).

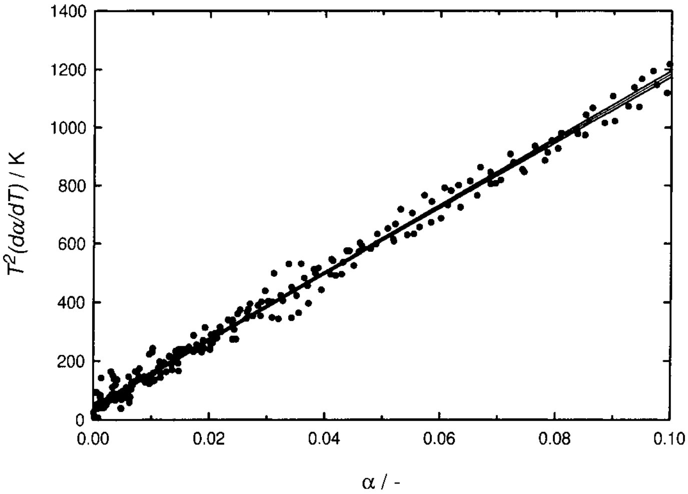

Fig. 4. Typical plot for the estimation of the E based on the initial rate method.

Thus, the basic prerequisite underlying the methods is satisfied. Furthermore, the linear model has been carefully checked in each regression procedure by means of the above mentioned statistical tests. This systematic approach substantiates the reliability of the E values. The differences between the results from each isoconversion method can be explained by the integral and differential forms of the respective equations. In the integral case, the results are influenced by the preceding reaction process while the differential method is more sensitive to the rate of the process. Despite the Ozawa–Flynn–Wall method being less accurate than the Friedman method, the results confirm its validity for the process under study.

Several studies [17,19,20] on the kinetics and mechanisms of the thermal decomposition of AN have revealed that the main products N_2O and H_2O result from the exothermic decomposition reaction

$$NH_4NO_3(l) \rightarrow N_2O(g) + 2H_2O(g)$$

However, the usual thermal behavior of small samples of AN on heating is not typical of an exothermic reaction. This has been explained by the occurrence of the endothermic dissociation reaction

$$NH_4NO_3(l) \rightarrow NH_3(g) + HNO_3(g)$$

which is coupled with the decomposition reaction. This coupling is both kinetic and thermal. The thermal behavior (endothermic or exothermic) that prevails in the overall process depends on several experimental factors [17,20]. In the absence of conditions favorable to the occurrence of an auto-catalytic regime and a consequent thermal run-away, the heat produced by the exothermic decomposition as well as heat supplied by an external source if exists may be absorbed by the dissociation reaction. This can explain the observed endothermic peaks in DSC curves referred to AN.

The experimentally resolved DSC/TG curves do not permit a detailed insight on the possible elementary steps occurring during the thermal decomposition of PSAN. Any possible influence of the additives intrinsic to PSAN (NiO, Petro) would not be strong enough to be unequivocally identified in the thermoanalytical curves, since the global patterns of the DSC/TG curves are similar to those found in other thermal analysis studies [23,24] using AN without additives. Thus it would be reasonable to admit that the above described major reaction steps and respective thermal effects that have been identified in the thermal decomposition of AN may also hold for PSAN.

Fig. 3 shows a slight decrease of E near the lower conversion limit. This tendency agrees with the somewhat higher value of E obtained from the initial rates method. This can be related not only with the melting process but also with some change in the overall reactive process. The activation energy should be viewed as composite quantity reflecting the temperature dependence of the rate constants of each indivi-

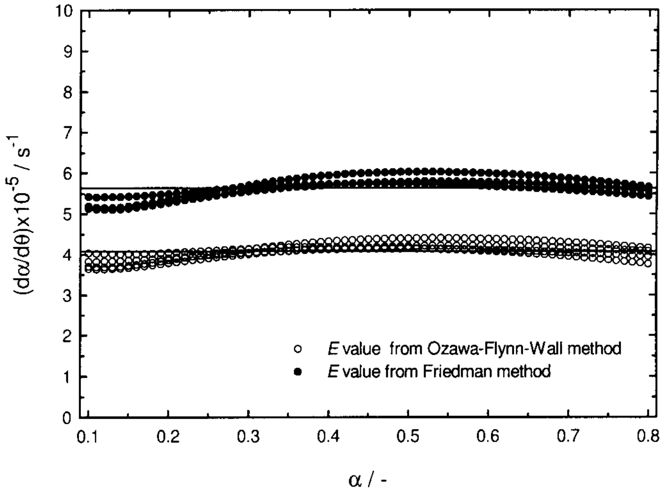

Fig. 5. Plot of dα/dθ against α in the range of kinetic analysis (horizontal lines correspond to the mean values).

dual reaction. In the early stage of the process, the heat available for the endothermic dissociation is mainly supplied by an external source. However, as soon as the exothermic decomposition becomes important a new source of heat becomes available. These possible changes in the kinetic and thermal coupling between the two main reactions can explain the observed variation of E at lower conversions. The smaller magnitude of the variation of E at the higher conversion levels indicates that the individual rates of the dissociation and decomposition reactions would be comparable. Thus the overall rate constant can be expressed by the Arrhenius equation in good approximation.

The average value of E over the conversion range 0.10–0.80 has been used to determine the term dα/dθ according to Eq. (9). The plot dα/dθ against α is shown in Fig. 5. Since dα/dθ is approximately constant for $0.10 \leq \alpha \leq 0.80$ the process is well described by the one-dimensional phase-boundary reaction kinetic model (R1), that is $f(\alpha) = 1$. Thus, the value of A is given directly by the constant corresponding to dα/dθ. Such as observed for E, the invariance of A with α over the range of the kinetic analysis validates the applicability of Eq. (1). Table 3 summarizes the results of this analysis as well as the results obtained by Koga and Tanaka [23,24] in which AN as been used to study the effect of the sample mass on the kinetics of the decomposition under isothermal and non-isothermal conditions.

Table 3
Arrhenius parameters for the thermal decomposition of PSAN and AN

Ref.	E (KJ mol^{-1})	log(A/s^{-1})	Obs.
This work	80.0±2.8[a] 81.4±3.5[b]	5.61±0.01 5.75±0.01	Non-isothermal (2.13±0.05) mg of PSAN
[24]	97.9±0.5	7.47±0.01	Non-isothermal 5.0 mg of AN
[23]	88.6±2.7	6.6±0.3	Isothermal (2.59±0.03) mg of AN

[a] Estimated from the Ozawa–Flynn–Wall method.
[b] Estimated from the Friedman method.

Table 3 shows an acceptable agreement in the Arrhenius parameters between the results obtained in this work and those reported by Koga and Tanaka [23] in which isothermal conditions have been employed, while the reported results corresponding to the non-isothermal [24] are somewhat different. A discussion in terms of the reproducibility of results should take into account a considerable number of factors. The particular characteristics of the samples (AN or PSAN, particle size distribution) are one of these factors but others that exist would also play an important rule and are to be considered to justify differences in the Arrhenius parameters [37]. As shown in Table 3, appreciably different sample mass has been used in each study, and it is well-known that this is an important factor in the kinetic analysis based on thermoanalytical data. This has been demonstrated for the particular case of AN by the works of Koga and Tanaka [23,24]. In this context they have proposed a methodology to obtain the 'specific activation energy,' a quantity independent of sample mass, being the reported values 86.2±2.0 and 97.1±0.1 kJ mol^{-1}, respectively for the isothermal and the non-isothermal cases. The first one is even closer to the obtained values for PSAN.

A relatively small sample mass has been used in the study of the thermal decomposition of PSAN. Thus, the self-generated reaction conditions, temperature gradients in the reactive mass, and other factors whose effects are usually connected with the sample mass, have been minimized. Reducing this physical effects the kinetic analysis appears to be more reliable. In short, it is our belief that the Arrhenius parameters characterizing the thermal decomposition of PSAN, as obtained by the applied isoconversion methods, are reliable values to describe the process. The inadequacy of the single curve method also applied, considering a first-order kinetics as reported in other works in which different experimental conditions have been employed, has been clearly demonstrated. Assuming that the 'specific Arrhenius parameters' reported for the decomposition of AN [23,24] may be used as reference values for comparative purposes, it is apparent that the small amounts of additives characterizing the particular type of PSAN used in this study do not have a dramatic influence on its thermal behavior when compared with AN.

5. Conclusion

Depending on the possible processes and/or stabilizing agents underlying its preparation, and consequently on the related factors such as the thermal history, particle morphology, and/or presence of additives, the thermal behavior of PSAN may exhibit departure from, what is known in the case of AN. The global consistence of the obtained results for the particular type of PSAN used in this work permitted to elucidate its thermal behavior and to conclude that no dramatic differences regarding AN without additives are detectable in the light of the macroscopic nature of the thermoanalytical curves.

The use of simple methods in the kinetic analysis based on single thermoanalytical curves is prone to lead to meaningless results. This is particularly critical when inadequate assumptions are made, namely those based on previously reported kinetic data on the thermal decomposition of virtually comparable materials. This has been confirmed by applying a single curve method considering a first-order reaction kinetic model for the thermal decomposition of PSAN. Values for E ranging from 100 to 113 kJ mol^{-1} depending on the range of the kinetic analysis were obtained. A more careful checking of the mathematical modeling allowed us to conclude on its inadequacy and thus on the meaningless of the kinetic information derived from it. On the contrary, the application of isoconversion methods allowed to reach a value of E close to 81 kJ mol^{-1} whose reliability was confirmed by the fulfilment of the prerequisites underlying the methods. This permitted to proceed with the kinetic analysis in the range of α from 0.10 to 0.80, to conclude that the process was well described by the one-dimensional phase boundary reaction kinetic model (R1), and to obtain a value for A close to 5.6×10^5 s^{-1}. The credibility of the quantitative characterisation of the thermal decomposition of PSAN under the conditions studied is substantiated by the wealth of the thermoanalytical data employed as well as on its systematic statistical treatment.

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