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SIGNIFICANCE OF NON-ISOTHERMAL KINETIC DATA
A statistical study

F. Rodante and S. Vecchio

Dipartimento di Ingegneria Chimica dei Materiali delle Materie Prime e Metallurgia, Università 'La Sapienza', Via del Castro Laurenziano 7, 00161 Roma, Italy

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Abstract

Arrhenius parameters values, in non-isothermal kinetic vaporisation processes for a series of compounds with related structures, have been calculated. This was made using a method of calculation that allows to find the most probable vaporisation mechanisms.

According to this method DTG curves were compared with some theoretical ones reported in literature, whose shape results to be only a function of the mechanisms. In this way the choice of the mathematical functions which can be inserted in the kinetic equations, was influenced by the shape of the DTG plots and other thermal analysis signals thus allowing to choose the most probable mechanisms.

The kinetic parameters derived from these mechanisms were compared, using statistical analysis, with those obtained from another method of calculation based on 'a priori' vaporisation mechanism chosen for the investigated liquid–gas transition.

The standard deviations of the slope and of the intercept, together with the standard deviation and the square correlation coefficient (r^2) of the linear regression equations related to the mechanisms of the two methods were calculated. Student *t*-test, Fisher *F*-test, confidence intervals (*c.i.*) and residuals values were also given.

Statistical analysis shows that the mechanisms obtained with the former method (diffusive and geometrical models) and the related Arrhenius parameters result to be more significant (in terms of probability) than the corresponding quantities of the latter for which a first-order model was chosen.

Keywords: Arrhenius equation, linear regression analysis, non-isothermal kinetics method of calculation, Satava equation, 1,3,5-triazine derivatives

Introduction

The Arrhenius parameters related to solid–gas-phase transition in non-isothermal kinetic processes show two drawbacks of some importance. The former is related to the reproducibility of these quantities the latter to their physical meaning.

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Both these effects for the mentioned processes occur because, for example, the choice of the mathematical functions $f(\alpha)$ which can be insert in the following equation

$$\frac{d\alpha}{dT} = \frac{A\exp\left(-\frac{E}{RT}\right)f(\alpha)}{\beta} \quad (1)$$

is made by the experimenter. In this equation, α is the degree of conversion (reaction progress), A the pre-exponential factor (s^{-1}), β is the heating rate (K min^{-1}), E is the activation energy (kJ mol^{-1}), R the gas constant (8.3145 J K^{-1} mol^{-1}) and T the temperature (K).

However rearranging Eq. (1) the Arrhenius equation can be obtained:

$$\ln\frac{\left(\frac{d\alpha}{dT}\right)\beta}{f(\alpha)} = \ln k = \ln A - \frac{E}{RT} \quad (2)$$

from which the calculation of Arrhenius parameters is carried out, both according to the differential or integral methods, by inserting the mathematical functions which describe the most probable mechanisms.

This procedure is one of the causes that determine different values of the Arrhenius parameters for the same compounds in the same processes.

Zsakó [1–4] affirms that calculation techniques aiming at deriving kinetic parameters are in fact variational methods, allowing us to obtain the non-isothermal apparent parameters (E, A, n-order) that ensure the best fit of kinetic equations to the experimental TG curves.

According to this author these quantities have not a clear physical meaning but they are kinetic parameters of a hypothetical nth-order homogeneous reaction which best simulates the experimental TG curves.

Unfortunately, in most of those kinetic equations it is assumed that the closer the value of r (correlation coefficient) is to the unity, the better would be the fit of the linear regressions with respect to the results.

However one must consider that the r value is only a guide to the significance of any apparent correlation between two random variables in a mathematical function that could not be linear.

It is well known, for instance, that in some chemical-physical problems (i.e. Hammet and Arrhenius equations) a physical significance is usually assigned (using both r and standard deviation) to the regression parameters (i.e. activation energy E) without an evaluation of its error estimation significance.

With regards to this fact Galway and Brown [5, 6] write that in most of kinetic studies of solid state decompositions the accuracy of the activation energy values E is frequently difficult to assess. Reproducibility of measurements is not always good and relatively few values have been confirmed independently.

E values have been often reported by using several significant figures, without the provision of realistic estimates of the measurements uncertainties. Moreover the Arrhenius plots are generally assumed to be linear for solid state reactions and few tests are made for possible deviations.

It is then interesting to use linear regression analysis which supplies the precise form of the mathematical function relating to the two variables, and tests how the experimental results support the theoretical relationship within the limits of the experimental error of the measurements. In this context, more useful tests are the standard deviation on the slope σ_b and on the intercept σ_a, the standard deviation of the regression $\sigma_{y/x}$, the Student *t*-test of the intercept, the slope values of the linear regression [7–12], and the Fisher *F*-test that makes a comparison between the standard deviations of two linear regression equations.

Furthermore it must be recalled that a statistical analysis cannot provide absolute answers, but only allows the experimental results to be compared and explained in terms of probability. Indeed, for this kind of analysis, an introduction of absolute data (confidence level, error distribution, etc.) is needed to explain the results in positive or negative ways.

This work aims at stressing significant Arrhenius parameters values, in non-isothermal kinetic vaporisation processes, for a series of compounds with related structures. This can be made using a method of calculation which allows to find the most probable vaporisation mechanisms. The kinetic parameters derived from these mechanisms can be compared to those calculated, for the same compounds, by means of a method of calculation based on a single mechanism chosen a priori [13]. This comparison is possible using the statistical analysis.

Experimental

The 1,3,5-triazine derivatives studied (Polyscience) were used without purification and their purity (99%) is larger than that needed for the application of DSC. The purity of the compounds was checked by HPLC measurements. Their common names and the chemical classifications are listed in Table 1.

The experimental measurements were carried out on a Stanton Redcroft 625 simultaneous TG-DSC instrument connected to an Olivetti 250 computer.

As regards the calibration of temperature the use of several standard allows the determination a linear temperature function. This function is used to calculate the correction to be added to the sample temperature.

As concerns DSC calibration, after production of a baseline curve with sapphire, subsequent experiments are used to convert the raw data counts to rates of heat transfer. Calibration experiments on the fusion of standard materials (lead, tin, zinc, benzoic acid) are used to 'fine tune' the data collected.

For decomposition studies under dynamic conditions, the TG-DSC apparatus was set up as follows: samples (6–8 mg) were weighed in aluminium pans. To avoid oxidative decomposition of the samples, the TG-DSC system was flushed with nitrogen gas both below (at a flow rate of 50 ml min^{-1}) and above (at a flow rate of

30 ml min^{-1}) the open pan. In this way, the gases evolved during the thermal decomposition experiments were removed continuously. The heating rate was always 10 K min^{-1} and at least two runs were made for each compound.

Table 1 Name, chemical specification and symbol of some pesticides

Symbol	Compounds	Nomenclature
a	Anilazine	1,3,5-triazine-2-amine, 4,6-dichloro-N-(2-chlorophenyl)
b	Ametryn	1,3,5-triazine-2,4-diamine, N-ethyl-N'-(1-methylethyl)-6-(methylthio)
c	Metribuzin	1,2,4-triazine-5(4H)-one, 4-amino-6-(1,1-dimethylethyl)-3-methylthio)
d	Dipropetryn	1,3,5-triazine-2,4-diamine, 6-(ethylthio)-N,N'-bis(1-methylethyl)
e	Cyromazine	N-cyclopropyl-1,3,5-triazine-2,4,6-triamine
f	Simetryn	1,3,5-triazine-2,4-diamine, N,N'-diethyl-6-(methylthio)
g	Trietazine	1,3,5-triazine-2,4-diamine, 6-chloro-N,N,N'-triethyl
h	Terbutylazine	1,3,5-triazine-2,4-diamine, 6 chloro-N-(1,1-dimethylethyl)-N'-ethyl
i	Terbutryn	1,3,5-triazine-2,4-diamine, N-(1,1-dimethylethyl)-N'-ethyl-6-(methylthio)

All the thermodynamic quantities were calculated by using the Stanton–Redcroft Acquisition System Trace, version 4.

Thermal Analysis included the extrapolated temperatures of decomposition onset, the percentage mass losses and the enthalpy values of the various processes (melting, crystallization, polymorphic changes, decomposition, chemical reactions) occurring as the temperature was raised.

During heating, all compounds can undergo a solid–liquid-phase transition (without molecular decomposition) and a liquid–gas-phase transition (with possible molecular decomposition).

The gaseous products of thermal processes were adsorbed into carbon trap adsorbent tubes (Supelco), desorbed into an organic liquid (CS_2) and injected into Hewlett-Packard 5890 GC coupled to a Hewlett-Packard MS 5971 Selective Detector. The capillary column used was a PTE, 30 m length×0.25 mm id, with a stationary phase film thickness of 0.25 μm (Supelco).

The GC oven was held at 343.15 K for 2 min, then was ramped at 10 K min^{-1} to 553.15 K. The carrier gas (helium) flow was 0.8 ml min^{-1}.

MS determination was performed with the SCAN technique using electron impact ionization at 70 eV, and transfer line was maintained at 553.15 K.

The total ion current chromatograms (TICS) and the relative spectra of the gaseous products were recorded. The mass spectra throughout the scanning range were compared with those of the pure compounds reported in the literature. By considering this experimental evidence, it can be concluded that all the studied compounds underwent liquid–gas-phase transition processes without decomposition.

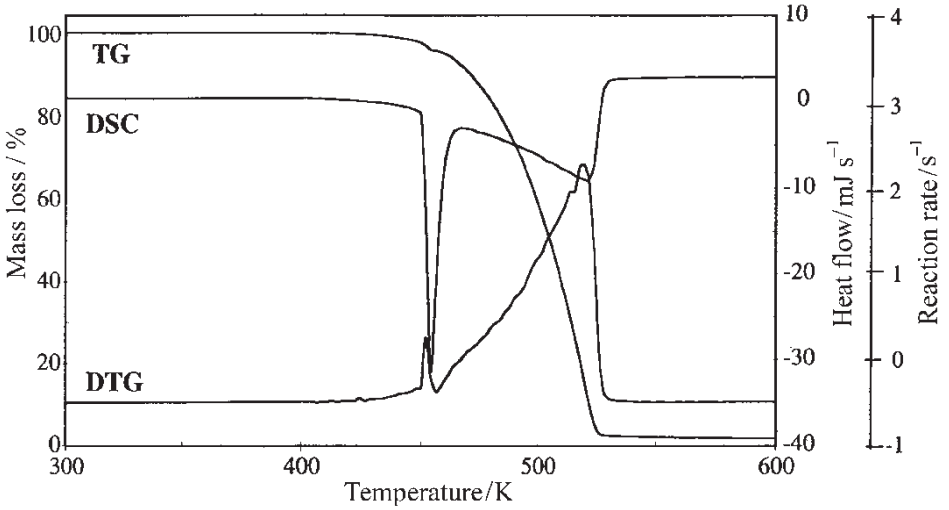

Fig. 1 TG/DTG/DSC curves for terbutylazine

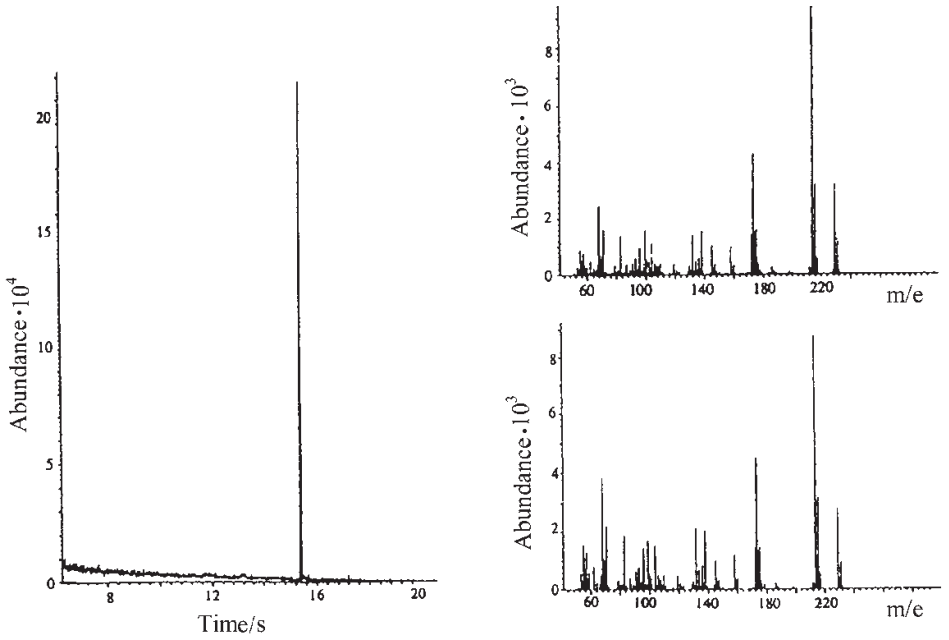

Fig. 2 Total Ion Current (TIC) chromatogram and mass spectra of terbutylazine

For instance the TG/DTG/DSC curves, the TIC chromatogram and the relative mass spectra for the gaseous products and the pure terbutylazine are reported in Figs 1 and 2 respectively.

Procedure

The kinetics of the liquid–gas phase transition processes based on dynamic TG technique was carried out for the compounds studied by the method of McCarty–Green [14]. The non-isothermal kinetic analysis included the calculation of activation energy E related to the phase transition processes, the pre-exponential factor A, and the reaction order. This implementation of the McCarty–Green method is restricted to the reactions of the first-order. The starting equation for this method assumes that in Eq. (1) $f(\alpha)=1-\alpha$, thus:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)(1-\alpha) \tag{3}$$

Rearranging Eq. (3) and integrating yields

$$-\ln(1-\alpha)=\left(\frac{AE}{\beta R}\right)p(x) \tag{4}$$

where x is the substituted variable for the quantity E/RT, and $p(x)$ represents a series expansion approximating the resulting integral:

$$p(x)\cong\left(\frac{x+3}{x(x+1)(x+4)e^{x}}\right) \tag{5}$$

On taking natural logarithms of both sides of Eq. (4) one can obtain

$$\ln(-\ln(1-\alpha))=\ln\left(\frac{AE}{\beta R}\right)+\ln p(x) \tag{6}$$

Assigning $F(\alpha)=\ln(-\ln(1-\alpha))$ and then differentiating with respect to x:

$$\frac{dF(\alpha)}{dx}=\frac{d\ln p(x)}{dx} \tag{7}$$

Substituting for x where $dx/d(1/T)=E/R$ yields

$$E=R\frac{\dfrac{dF(\alpha)}{d(1/T)}}{\dfrac{d\ln p(x)}{dx}} \tag{8}$$

The data for the construction of this plot are taken from the TG curve. The numerator in Eq. (8) is the slope of a plot of $F(\alpha)$ *vs.* $1/T$ whereas the denominator can be estimated from the series

$$\frac{d\ln(p(x))}{dx}=\frac{1}{x+3}-\frac{1}{x}-\frac{1}{x+1}-\frac{1}{x+4}-1$$

Since the numerator is also a function of E, the software uses an initial guess of 125.56 kJ mol^{-1} for the activation energy. A series of iterative calculations is performed to refine the value of E to within 0.42 J. Once E has been determined, the pre-exponential factor A is calculated by the Eq. (4). This study considered mass losses consistently lower than 10% for the calculation of activation energy.

Indeed, it was usually considered [15] that the initial portion of the TG curves can be fitted by a first-order reaction equation. The Arrhenius parameters values (A and E) obtained using this integral method are a function of F_1 mechanism (first-order reaction).

Nevertheless in order to study chemical and physical properties variation related to non-isothermal processes it has become usual to associate mathematical relationship with a particular model of mechanism but there are several models giving the same mathematical expression and the same model giving two, three or more alternative expressions.

Dollimore and co-workers [16–19] have developed a computer program that plots a theoretical $d\alpha/dT$ curve by using the Eq. (1) when the hypothesized mechanism $f(\alpha)$ and the suitable values of both A and E are introduced.

This approach may be considered as the reverse of the Arrhenius non-isothermal kinetics in which A and E are calculated from α-T plots and by assuming a proper mechanism. The shape of the theoretical curve obtained in this way proves to be only a function of the mechanism and makes it possible to determine the following parameters:

I. the starting (T_i) and final (T_f) temperatures of the TG curve as diffuse (d) or sharp (s).

II. the half width defined as the peak width on the differential plot of $d\alpha/dT$ *vs.* T measured at half height.

III. the value of α_{max} at the maximum rate of the process (at T_p) in the α-T plot.

The comparison of these characteristic quantities (half width, α_{max}, T_i, and T_f) for our experimental curves with those reported in literature [16, 17] shows more than one possible mechanism for each compound.

In order to select the appropriate mechanism for each compound and to determine the kinetic parameters A and E, the following method was used.

The α values, calculated from TG curves as a function of the temperature, together with those of $d\alpha/dT$ (the reverse of DTG), were inserted in the mathematical expressions of $f(\alpha)$ and used in the Arrhenius differential Eq. (2).

The α values were also inserted in the mathematical expression of integral conversion function $g(\alpha)$ and used in the Satava [20] integral equation

$$\log[g(\alpha)] = -0.4567\frac{E}{RT} - 2.315 + \log\frac{AE}{R\beta} \tag{9}$$

where Doyle's approximation is valid in a temperature range of 100 K [21].

From Eqs (2) and (9) the Arrhenius parameters can be calculated by the following linear relationships

$$\ln\frac{\left(\frac{d\alpha}{dT}\right)\beta}{f(\alpha)} \; vs.\; 1/T \tag{10}$$

$$\log[g(\alpha)] \; vs.\; 1/T \tag{11}$$

where $f(\alpha)$ and $g(\alpha)$ are the mathematical expressions related to the mechanisms according to the two methods.

From the regression coefficient and the intercept of the regression straight lines, the E and A parameters were calculated. Subsequently, the linear regression functions, which depend on the different mechanisms, were submitted to a statistical analysis.

Together with the standard deviation, the Student t-test, related to the regression coefficient (slope) and to the intercept, ensures the linearity of the relationship and allows to calculate, in terms of probability, the confidence intervals *c.i.* ($E\pm\sigma_E t_{CL,v}$, $A\pm\sigma_A t_{CL,v}$) caused by the variability of the experiments. In the mentioned intervals, the true values of the regression function parameters (regression coefficient b, intercept a and the estimated values y') could lie with a fixed degree of probability.

The regression standard deviation $\sigma_{y/x}$ (which is the fundamental parameter to evaluate the linear degree between the two variables) cannot be directly related to the accuracy and reproducibility of the experimental points y but allows to find them, in terms of probability, within the two scattering bands formed by the $y'\pm\sigma_{y/x}$ straight lines around the regression equation.

Finally the values of A, E and related mechanisms represented by $f(\alpha)$ were inserted in Eq. (1) and the theoretical DTG curves are reconstructed and compared with the experimental ones.

During heating, all the compounds undergo both solid–liquid and liquid–gas phase transitions without decomposition as seen by the GC-MS measurements.

The thermodynamics of the processes regarding the compounds which exhibit only liquid–gas-phase transition (without decomposition) could be examined assuming that the system attains equilibrium at any stage.

When the equilibrium is achieved, the extent of the mass loss (measured by the α values at a given temperature) could be described by the ratio of the equilibrium rate pressure p to the atmospheric $p°$.

The vaporization process could be described by the integral of the Clausius–Clapeyron equation

$$\int_{p}^{p^\circ}\frac{dp}{p}=\frac{\Delta H_v}{R}\int_{T}^{T_v}\frac{dT}{T^2} \tag{12}$$

Solving the integral the equation becomes

$$\ln\frac{p}{p^\circ}=\ln\alpha=\frac{\Delta H_v}{RT_v}-\left(\frac{\Delta H_v}{R}\right)\frac{1}{T} \tag{13}$$

where T_v and ΔH_v are related to vaporisation process and $p°$ is the pressure at vaporisation temperature T_v. Substituting the experimental α values to $p/p°$ and plotting $\ln\alpha$ *vs.* $1/T$ one can determine ΔH_v and T_v from the slope and the intercept of a linear regression analysis respectively.

The approximate nature [10] of the linear Clausius–Clapeyron can be tested by comparing the linear regression related to this equation with that related to Arrhenius equation.

This procedure was carried out stating the hypothesis that between the enthalpy values obtained from Eq. (13) and the activation energy values calculated from the Eq. (2) a significant difference does not exist.

Results and discussion

Kinetic data relative to TG curves of liquid–gas processes for studied compounds obtained by McCarty–Green method are reported in Table 2. These values are related to a mechanism described by the mathematical expression $f(\alpha)=1-\alpha$ and so they are limited to F_1 mechanism.

Table 2 Kinetic parameters of liquid–gas phase transition processes of 1,3,5-triazine derivatives according to McCarty and Green equation [14]

Compound	E/kJ mol^{-1}	$\ln A/s^{-1}$
Anilazine	59.12	16.25
Ametryn	63.68	16.94
Metribuzin	65.12	17.39
Dipropetryn	60.89	16.86
Cyromazine	63.08	16.53
Simetryn	62.89	17.23
Trietazine	60.95	17.34
Terbutylazine	67.21	18.71
Terbutryn	67.95	18.40

It is shown that α_{max} is characteristic of any specific mechanism and practically does not depend on the Arrhenius parameters and on the heating rate β.

With further information offered by the width of the peaks of the DTG curves at half-height (the so-called half-width) it is usually possible to increase the choice of the proper mathematical expression which describes the transformation examined.

To this purpose all parameters related to the evaluation of mechanism of liquid–gas phase trasition taken from TG/DTG curves are reported in Table 3.

All the compounds examined show the same typical TG/DTG shapes:

TG curves with a diffuse initial or onset temperature and a sharp final one; DTG curves with a ratio $\Delta T_{lo}/\Delta T_{hi}$ (which represents the asymmetry of the DTG curves) always greater than the unity.

Table 3 Parameters related to mechanism-characteristic features for the liquid–gas phase transition processes of 1, 3, 5 triazine derivatives obtained from TG/DTG curves

Compound	From TG curves		From DTG curves				
	Characteristic features of T_i and T_f	α_{max}	T_i/K	T_f/K	$\frac{\Delta T_{L0}}{\Delta T}$	Half width/K	Kinetic model
Anilazine	T_i diffuse. T_f sharp	0.75	458.2	580.0	2.4	34.1	D_2, R_2
Ametryn	T_i diffuse. T_f sharp	0.88	472.2	564.1	6.0	35.1	D_2, R_2
Metribuzin	T_i diffuse. T_f sharp	0.74	475.1	613.2	3.2	41.8	D_2, R_2
Dipropetryn	T_i diffuse. T_f sharp	0.90	457.0	549.1	7.6	36.3	D_2, R_2
Cyromazine	T_i diffuse. T_f sharp	0.82	508.0	604.0	4.3	42.0	D_2, R_2
Simetryn	T_i diffuse. T_f sharp	0.83	462.2	550.2	4.3	37.1	D_2, R_2
Trietazine	T_i diffuse. T_f sharp	0.89	445.0	535.0	6.2	21.0	D_2, R_2
Terbutylazine	T_i diffuse. T_f sharp	0.83	461.0	539.1	4.7	33.9	D_2, R_2
Terbutryn	T_i diffuse. T_f sharp	0.88	469.1	549.1	6.8	32.2	D_2, R_2

By comparing our experimental α_{max} and half-width values with the theoretical ones reported in the literature by Dollimore and co-workers [17], one can conclude that only the following mechanisms are possible: D_2, R_2.

The mathematical expressions $f(\alpha)$ (used in differential method) and $g(\alpha)$ (used in the Satava integral method) for the most probable mechanisms are reported in Table 4.

Table 4 Classification of mathematical expressions of possible reaction mechanisms

Kinetic classification	$f(\alpha)=(1/k)(d\alpha/dT)\beta$	$g(\alpha)=\int d\alpha/f(\alpha)=kt$
Diffusion mechanisms		
D_1 one-dimensional	$1/2\alpha$	α^2
D_2 two-dimensional	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D_3 three-dimensional	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
Based on geometrical models		
R_2 contracting area	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R_3 contracting volume	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Based on the 'order of reaction'		
F_1 first-order	$(1-\alpha)$	$-\ln(1-\alpha)$

From TG curves the plots of the degree of conversion α *vs.* temperature (K) were constructed. The $d\alpha/dT$ values, obtained from the DTG ones, the heating rate β and the mathematical expressions of $f(\alpha)$ and $g(\alpha)$ describing D_2, R_2 and F_1 mechanisms were inserted in Eqs (2) and (9).

The kinetic data extrapolated from the linearization of Arrhenius and Satava equations for the hypothesized mechanisms are reported in Table 5.

Table 5 Kinetic parameters extrapoled from linearization of Arrhenius and Satava equations at *CL*=0.995

Compound	Model	Arrhenius equation		Satava equation	
		E/kJ mol^{-1}	ln$A$/s^{-1}	E/kJ mol^{-1}	ln$A$/s^{-1}
Anilazine	D_2	153.0	37.2	156.6	38.2
	R_2	77.3	19.1	80.5	21.0
	F_1	91.4	24.1	87.4	23.6
Ametryn	D_2	167.1	39.8	171.1	40.9
	R_2	81.5	20.3	87.4	22.0
	F_1	92.3	24.1	92.8	24.0
Metribuzin	D_2	180.4	42.9	187.5	44.5
	R_2	84.8	21.3	94.7	23.8
	F_1	94.8	24.5	98.3	25.6
Dipropetryn	D_2	170.4	42.0	176.6	43.9
	R_2	80.6	21.0	89.2	23.6
	F_1	90.6	24.1	94.7	25.4
Cyromazine	D_2	203.7	45.2	187.5	41.5
	R_2	112.2	26.1	96.5	22.6
	F_1	130.5	31.1	130.8	25.1
Simetryn	D_2	141.3	35.1	167.5	40.7
	R_2	74.8	19.1	87.4	22.7
	F_1	108.1	29.1	101.9	26.9
Trietazine	D_2	124.7	31.1	162.0	41.0
	R_2	58.2	16.1	85.6	23.0
	F_1	108.1	29.1	101.9	28.1
Terbutylazine	D_2	141.3	35.1	194.8	47.7
	R_2	66.5	18.1	103.8	26.9
	F_1	124.7	34.1	125.6	33.4
Terbutryn	D_2	183.7	44.6	183.5	44.6
	R_2	93.9	24.1	94.3	24.0
	F_1	108.1	29.1	101.9	26.9

Both Eqs (2) and (9) can be represented by a linear equation:

$$y=a+bx$$

where according to Arrhenius equation

$$a=\ln A;\ b=-\frac{E}{R};\ x=\frac{1}{T};\ y=\ln\frac{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\beta}{f(\alpha)}$$

while according to Satava equation

$$a=-2.135+\log\left(\frac{AE}{R\beta}\right);\ b=-0.4567\frac{E}{R};\ x=\frac{1}{T};\ y=\log[g(\alpha)]$$

Obviously the E and A values obtained inserting the expressions pertaining to F_1 mechanism in the Arrhenius and Satava equations do not agree with those extrapolated from the McCarty–Green method. In order to test the significance of the regression parameters related to the three mechanisms considered (D_2, R_2 and F_1) a statistical analysis was carried out.

According to the linear relationships (10) and (11) the values of regression parameters a and b together with their standard deviations σ_a and σ_b, the confidence intervals (*c.i.*), the degree of freedom ν and the square correlation coefficient r^2 are given in Tables 6 and 7 respectively. At fixed values of α the same quantities of the estimated values y' for some of the studied compounds are given in Table 8.

Table 6 Statistical parameters related to least-square method of linear regression analysis applied to Arrhenius equation for 1,3,5-triazine derivatives studied according to different mechanism $f(\alpha)$

Compound	Model	Intercept			Slope			ν	r^2
		a	σ_a	$c.i._{0.995}$	b	σ_b	$c.i._{0.995}$		
Anilazine	D_2	33.1	0.233	±0.6	–18.4	0.114	±0,3	43	0.9983
	R_2	15.0	0.363	±1.0	–9.3	0.177	±0,5		0.9844
	F_1	20.0	0.753	±1.0	20.0	0.367	±1.0		0.9957
Ametryn	D_2	35.7	0.210	±0.5	–20.1	0.101	±0,3	66	0.9983
	R_2	15.0	0.238	±0.6	–9.8	0.115	±0,3		0.9910
	F_1	20.0	0.598	±1.0	–11.1	0.288	±0,8		0.9574
Metribuzin	D_2	38.8	0.247	±0.6	–21.7	0120	±0,3	56	0.9983
	R_2	17.2	0.086	±0.2	–10.2	0.041	±0,1		0.9991
	F_1	20.4	0.309	±0.8	–11.4	0.150	±0,4		0.9904
Dipropetryn	D_2	37.9	0.338	±0.9	–20.5	0.159	±0,4	57	0.9966
	R_2	16.9	0.201	±0.5	–9.7	0.095	±0,2		0.9946
	F_1	20.0	0.472	±1.0	–10.9	0.222	±0,6		0.9771
Cyromazine	D_2	41.1	0.351	±0.9	–24.5	0.190	±0,5	37	0.9978
	R_2	22.0	0.408	±1.0	–13.5	0.221	±0,6		0.9901
	F_1	27.0	0.121	±1.0	–15.7	0.254	±0,7		0.9904
Simetryn	D_2	31.0	1.771	±5.0	–17.0	0.864	±2.0	56	0.8791
	R_2	15.0	1.061	±3.0	–9.0	0.518	±1.0		0.8454
	F_1	25.0	1.110	±3.0	–13.0	0.501	±1.0		0.9175
Trietazine	D_2	27.0	2.333	±6.0	–15.0	1.105	±3.0	53	0.7746
	R_2	12.0	1.370	±4.0	–7.0	0.649	±2.0		0.7124
	F_1	25.0	1.166	±3.0	–13.0	0.553	±1.0		0.9107
Terbutylazine	D_2	31.0	3.251	±9.0	–17.0	1.589	±4.0	45	0.7173
	R_2	14.0	1.838	±5.0	–8.0	0.899	±2.0		0.6547
	F_1	30.0	1.161	±3.0	–15.0	0.568	±1.0		0.9430
Terbutryn	D_2	40.5	0.201	±0.5	–22.1	0.099	±0.3	39	0.9992
	R_2	20.0	0.365	±1.0	–11.3	0.180	±0.5		0.9902
	F_1	25.0	0.826	±2.0	–13.0	0.408	±1.0		0.9652

Table 7 Statistical parameters related to least-square method of linear regression analysis applied to Satava equation for 1,3,5-triazine derivatives studied according to different mechanism $g(\alpha)$

Compound	Model	Intercept			Slope			ν	r^2
		a	σ_a	$c.i._{0.995}$	b	σ_b	$c.i._{0.995}$		
Anilazine	D_2	15.8	0.089	±0.1	–8.6	0.043	±0.3	43	0.9989
	R_2	8.0	0.053	±0.2	–4.4	0.026	±0.5		0.9985
	F_1	9.2	0.119	±0.3	4.8	0.058	±1.0		0.9937
Ametryn	D_2	17.0	0.157	±0.4	–9.4	0.075	±0.3	66	0.9958
	R_2	8.5	0.076	±0.2	–4.8	0.037	±0.3		0.9962
	F_1	9.4	0.105	±0.3	–5.1	0.050	±0.8		0.9935
Metribuzin	D_2	18.6	0.187	±0.5	–10.3	0.091	±0.3	56	0.9956
	R_2	9.3	0.085	±0.2	–5.2	0.041	±0.1		0.9965
	F_1	10.1	0.076	±0.2	–5.4	0.037	±0.4		0.9974
Dipropetryn	D_2	18.3	0.237	±0.6	–9.7	0.111	±0.4	57	0.9926
	R_2	9.2	0.109	±0.3	–4.9	0.051	±0.2		0.9939
	F_1	10.0	0.101	±0.3	–5.2	0.047	±0.6		0.9953
Cyromazine	D_2	16.9	0.160	±0.4	–10.3	0.087	±0.5	37	0.9974
	R_2	8.8	0.100	±0.3	–5.3	0.054	±0.6		0.9961
	F_1	10.7	0.168	±0.4	–5.7	0.091	±0.7		0.9907
Simetryn	D_2	15.8	0.086	±0.2	–9.2	0.042	±0.1	56	0.9988
	R_2	8.0	0.047	±0.1	–4.8	0.023	±0.06		0.9987
	F_1	9.2	0.244	±0.6	5.6	0.119	±0.3		0.9751
Trietazine	D_2	17.0	0.294	±0.8	–8.9	0.139	±0.4	53	0.9871
	R_2	8.5	0.140	±0.4	–4.7	0.066	±0.2		0.9895
	F_1	9.4	0.291	±0.8	–5.6	0.138	±0.4		0.9687
Terbutylazine	D_2	18.6	0.401	±1.0	–10.7	0.196	±0.5	45	0.9851
	R_2	9.3	0.153	±0.4	–5.7	0.075	±0.2		0.9923
	F_1	10.1	0.249	±0.7	–6.9	0.122	±0.3		0.9861
Terbutryn	D_2	18.3	0.052	±0.1	–10.1	0.026	±0.07	39	0.9997
	R_2	9.2	0.037	±0.1	–5.2	0.018	±0.05		0.9995
	F_1	10.0	0.121	±0.3	–5.6	0.060	±0.2		0.9956

Test of linearity

A test of linearity for a hypothesized linear regression can be obtained from its coefficient and intercept regression significance.

This can be made using two null hypotheses tested by the Student *t*-test.

The *t* values of *a* and *b* were calculated by the expressions

$$t_a = \frac{(a-A)}{\sigma_a};\ t_b = \frac{(b-B)}{\sigma_b}$$

where *a* and *b* are the intercept and the slope respectively of the regression equation, σ_a and σ_b their standard deviations, *A* and *B* prefixed values.

For A=0 and B=0 t_a and t_b calculated were compared to those of a handbook of statistical tables [22]. If $t_{calc}>t_{CL,\nu}$, where ν is the degree of freedom and CL the confidence level for the significance of the regression, then for CL<0.95 the null hypothesis is accepted (chemical hypothesis) while for CL>0.999 its rejection is highly significant.

The null hypotheses a=0 and b=0 for the three mechanisms (Table 5) of all the compounds are rejected with 99.5% of probability (significant) thus confirming the linearity of these regression equations.

The intercept and the regression coefficient from which E and A values were calculated are significantly different from zero.

Table 8 Estimated y' values obtained at fixed values of α together with their standard deviations $\sigma_{y/x}$ and their confidence intervals $c.i._{0.995}$ for some of the 1,3,5-triazine derivatives studied

Compound	Model	α	Arrhenius equation			Satava equation		
			y'	$\sigma_{y'}$	$c.i._{0.995}$	y'	$\sigma_{y'}$	$c.i._{0.995}$
Anilazine	D_2	0.25	–4.0	0.083	±0.2	–1.5	0.032	±0.09
		0.50	–2.6	0.083	±0.2	–0.8	0.032	±0.09
		0.75	–1.8	0.083	±0.2	–0.4	0.032	±0.09
	R_2	0.25	–3.3	0.131	±0.3	–0.9	0.019	±0.05
		0.50	–2.6	0.131	±0.3	–0.5	0.019	±0.05
		0.75	–2.1	0.131	±0.3	–0.3	0.019	±0.05
	F_1	0.25	–2.3	0.271	±0.7	–0.5	0.043	±0.1
		0.50	–1.4	0.271	±0.7	–0.1	0.043	±0.1
		0.75	–0.9	0.271	±0.7	0.1	0.043	±0.1
Ametryn	D_2	0.25	–4.9	0.141	±0.4	–1.5	0.105	±0.1
		0.50	–3.3	0.141	±0.4	–0.8	0.105	±0.1
		0.75	–2.4	0.141	±0.4	–0.4	0.105	±0.1
	R_2	0.25	–3.4	0.160	±0.4	–0.9	0.051	±0.1
		0.50	–2.7	0.160	±0.4	–0.5	0.051	±0.1
		0.75	–2.2	0.160	±0.4	–0.3	0.051	±0.1
	F_1	0.25	–2.5	0.401	±1.0	–0.5	0.070	±0.2
		0.50	–1.6	0.401	±1.0	–0.1	0.070	±0.2
		0.75	–1.1	0.401	±1.0	0.1	0.070	±0.2
Metribuzin	D_2	0.25	–4.8	0.130	±0.3	–1.4	0.099	±0.3
		0.50	–3.2	0.130	±0.3	–0.8	0.099	±0.3
		0.75	–2.2	0.130	±0.3	–0.3	0.099	±0.3
	R_2	0.25	–3.4	0.055	±0.1	–0.8	0.045	±0.1
		0.50	–2.6	0.055	±0.1	–0.5	0.045	±0.1
		0.75	–2.2	0.055	±0.1	–0.3	0.045	±0.1
	F_1	0.25	–2.5	0.198	±0.5	–0.5	0.040	±0.1
		0.50	–1.7	0.198	±0.5	–0.1	0.040	±0.1
		0.75	–1.1	0.198	±0.5	0.1	0.040	±0.1

Degree of significance

The standard deviations of parameters a, b and y', allow to determine the confidence level (*c.i.*) $a \pm \sigma_a t_{CL,\nu}$, $b \pm \sigma_b t_{CL,\nu}$, $y' \pm \sigma_y t_{CL,\nu}$ (Tables 6, 7 and 8) where there is the probability (100*CL*)% that the true values of the above cited parameters lie.

$t_{CL,\nu}$ is chosen from proper tables [22] at a *CL* level and for ν degree of freedom. A significative level can be obtained choosing *CL* values ranging from 0.99 to 0.999.

Significative interval does not indicate, for example, that b parameter is significant but that in the considered interval there is a probability ranging from 99% to 99.9% to find the true value of b. It is clear that the more the c.i. is narrowed, the more b could be discussed by statistical point of view in physical terms. For the studied compounds, both for Satava and Arrhenius equations, all the regression parameters of mechanisms D_2, R_2 and F_1 lie in significant intervals with 99.5% of probability (Tables 6, 7 and 8) with the exception of those of Simetryn, Trietazine and Terbutylazine calculated by the Arrhenius equation.

Standard deviation of regression

It was reminded that the standard deviations $\sigma_{y/x}$ of different regressions cannot be compared as such but must be referred to the ratio $\sigma_{y/x}/\Delta y$ (relative standard deviation) where Δy represents the interval of the experimental y values.

As previously seen the regression standard deviation $\sigma_{y/x}$ cannot indicate rigorously the statistical error which is able to estimate the dependent variable y' by means of the regression function.

The statistical significance of this quantity is directly connected with the probability to find the number of experimental points contained within scattering bands represented by the $y' \pm \sigma_{y/x}$ straight lines around the regression function [7].

Moreover the expression

$$100[(y - y')/\Delta y] \tag{14}$$

(where y represent the experimental data and y' the values of the regression function) gives the percentage of the experimental points contained in the above cited zone (Table 9).

For all the compounds (with exception of Symetrin, Trietazine and Terbutylazine) high percentage values from (14) are evident in Table 9 for D_2 and R_2 mechanisms (on the average greater than standard one (68.5%) [7, 10]) thus indicating the goodness of the fit for the regressions related to the above cited mechanisms describing the vaporisation processes. This behaviour occurs in smaller degree for F_1 mechanism, as can be seen by the low percentage values of (14).

Since D_2 and R_2 mechanisms resulted more significant than F_1, their Arrhenius and Satava regression equations were compared, by the statistical point of view, to that of Clausius–Clapeyron.

Table 9 Percentage of y values as obtained from relationship (14), standard deviation $\sigma_{y/x}$ and relative standard deviations $\sigma_{y/x}/\Delta y$ of the linear regressions

Compound	Model	Arrhenius equation			Satava equation		
		% (14)	$\sigma_{y/x}$	$\sigma_{y/x}/\Delta y$	% (14)	$\sigma_{y/x}$	$\sigma_{y/x}/\Delta y$
Anilazine	D_2	60.4	0.083	0.01	77.8	0.032	0.009
	R_2	56.2	0.129	0.03	60.0	0.019	0.01
	F_1	37.2	0.268	0.06	27.2	0.042	0.02
Ametryn	D_2	64.4	0.138	0.01	73.5	0.104	0.02
	R_2	100.0	0.156	0.03	77.9	0.051	0.02
	F_1	42.5	0.398	0.05	35.6	0.070	0.02
Metribuzin	D_2	80.0	0.127	0.01	81.8	0.097	0.02
	R_2	88.9	0.129	0.09	75.0	0.044	0.02
	F_1	39.9	0.162	0.03	29.6	0.040	0.01
Dipropetryn	D_2	62.2	0.185	0.02	86.7	0.129	0.02
	R_2	97.8	0.110	0.02	86.7	0.060	0.02
	F_1	36.2	0.262	0.04	45.6	0.056	0.02
Cyromazine	D_2	76.9	0.091	0.01	38.1	0.041	0.02
	R_2	89.7	0.106	0.03	36.9	0.026	0.02
	F_1	42.2	0.121	0.03	33.1	0.043	0.03
Simetryn	D_2	35.7	0.923	0.20	38.1	0.086	0.01
	R_2	15.3	0.553	0.20	36.9	0.025	0.01
	F_1	22.2	0.579	0.09	30.2	0.127	0.04
Trietazine	D_2	<5	1.155	0.20	20.6	0.146	0.03
	R_2	67.4	0.678	0.20	17.6	0.069	0.03
	F_1	12.2	0.577	0.02	10.4	0.144	0.01
Terbutylazine	D_2	<5	1.234	0.30	10.7	0.152	0.04
	R_2	5.3	0.698	0.30	14.3	0.058	0.03
	F_1	6.6	0.441	0.01	5.5	0.094	0.006
Terbutryn	D_2	12.7	0.061	0.007	89.7	0.016	0.004
	R_2	70.9	0.112	0.02	89.7	0.011	0.005
	F_1	6.3	0.253	0.04	8.3	0.037	0.01

For this purpose the latter equation was submitted to a statistical analysis (Table 10). The *c.i.* values obtained as previously described show that there are significant parameters values.

It can be noted that the relative regression standard deviations $\sigma_{y/x}/\Delta y$ (Table 10) are greater than at least one of those related to the Arrhenius and Satava equations (Table 9). Moreover the percentage values from (14) result to be less than the standard one [7, 10] thus confirming the approximate linear nature of this equation.

In order to compare the E (Table 5) and ΔH_v values (Table 11) obtained from Arrhenius and Clapeyron equations respectively the null hypothesis $b_1=b_2$, (b_1 and b_2 being the slopes of the two linear regressions) has been considered.

The t values are calculated by relationship $t_b(1, 2)=(b_1-b_2-A)/\sigma_{(b_1-b_2)}$ where $A=0$ and $\sigma_{(b_1-b_2)}$ is the standard deviation of slopes difference for the two regressions ($b_1=E/R$, $b_2=\Delta H/R$). The F-test was used to verify that the standard deviations of the

Table 10 Statistical parameters related to least-square method of linear regression analysis applied to Clausius–Clapeyron equation for 1,3,5-triazine derivatives studied

Compound	Intercept			Slope			$\sigma_{y/x}$	$\sigma_{y/x}/\Delta y$	Values from Eq. (14)	$\sigma_{y'}$	$c.i._{0.995}$	ν	r^2
	a	σ_a	$c.i._{0.995}$	b	σ_b	$c.i._{0.995}$							
Anilazine	18.0	0.508	±1.0	–9.8	0.248	±0.6	0.313	0.04	27.5	0.066	±0.2	63	0.9611
Ametryn	19.3	0.234	±0.6	–10.6	0.113	±0.3	0.162	0.02	48.5	0.201	±0.5	68	0.9924
Metribuzin	18.0	0.454	±1.0	–10.0	0.227	±0.6	0.380	0.05	82.5	0.191	±0.5	79	0.9611
Dipropetryn	21.0	0.401	±1.0	–11.1	0.188	±0.5	0.401	0.04	42.5	0.247	±0.6	62	0.9825
Cyromazine	20.0	0.322	±0.8	–11.7	0.167	±0.4	0.209	0.03	67.1	0.046	±0.1	68	0.9864
Simetryn	22.0	0.310	±0.8	–11.6	0.142	±0.4	0.253	0.03	67.1	0.137	±0.4	73	0.9893
Trietazine	21.0	0.418	±1.0	–10.7	0.191	±0.5	0.216	0.03	73.2	0.277	±0.7	53	0.9834
Terbutylazine	27.0	0.794	±2.0	–14.0	0.379	±1.0	0.313	0.03	18.2	0.324	±0.9	45	0.9679
Terbutryn	22.3	0.310	±0.8	–11.9	0.150	±0.4	0.312	0.04	26.8	0.098	±0.3	52	0.9918

two regressions are not different from a statistical point of view (Table 12). From the ratio of the two regression variances

$$F = \frac{(\sigma^2_{y/x})_1}{(\sigma^2_{y/x})_2}$$

where $(\sigma^2_{y/x})_1 > (\sigma^2_{y/x})_2$, the F values were calculated.

Table 11 Temperature and enthalpy values of vaporization processes as extrapoled from Eq. (13)

Compound	T/K	ΔH/kJ mol^{-1}
Anilazine	535.9	81.48
Ametryn	548.5	88.13
Metribuzin	544.6	83.14
Dipropetryn	527.4	92.29
Cyromazine	536.3	97.28
Simetryn	525.1	96.45
Trietazine	515.2	88.97
Terbutylazine	524.1	116.40
Terbutryn	537.0	98.94

The above mentioned values were compared to those of a handbook (F_{tab}) [22]: as $F_{calc} > F_{tab}$ at CL=0.99 one can conclude that the standard deviations of the two regressions cannot be considered significantly different. For the two mechanisms of all the compounds there are $t_{calc} > t_{CL,v}$ at the CL=0.995, so that the null hypothesis is rejected. The enthalpy and the E values can be considered significantly different thus confirming the different degree of the linear significance for the two regressions.

Finally the choice of the most suitable of the two hypothesized mechanisms can be made by inserting the A and E values obtained by the Arrhenius equation and the related mechanisms represented by $f(\alpha)$ in Eq. (1). The theoretical $d\alpha/dT$ curves are constructed and compared to the experimental ones. The comparison between experimental and reconstructed curves has been carried out by establishing the following features for the best fit: the values of α_{max} (α at the maximum of $d\alpha/dT$ *vs.* T curve) and half-width (temperature interval at half-height of the DTG peak).

From the comparison of the two groups of curves (Figs 3a–i) the best mechanisms seems to be: D_2 for Ametryn, Dipropetryn, Cyromazine Simetryn, Trietazine, Terbutylazine, Terbutryn; R_2 for Anilazine and Metribuzin .

In Figs 4a–i experimental $d\alpha/dT$ curves are compared with those obtained by inserting in Eq. (1) A and E values obtained by Satava equation and corresponding $g(\alpha)$ expressions. This comparison confirms the results obtained by Figs 3a–i.

Table 12 *t*- and *F*-tests applied to evaluate the significance of differences between regression coefficients of Arrhenius and Clausius–Clapeyron equations respectively for 1,3,5-triazine derivatives studied

Compound	Model	ν	*t* values calculated	t_{CL} values tabulated[a]			*F* values calculated	*F* values tabulated[c]
				$t_{0.995}$	$t_{0.95}$	$t_{0.75}$	Clapeyron/Arrhenius	Clapeyron/Arrhenius
Anilazine	D_2	43	–100.09	2.70	1.68	0.681	14.221	1.660 (40, 50)[b]
	R_2		5.82				5.887	
Ametryn	D_2	66	–450.02	2.39	1.67	0.679	1.378	1.599 (50, 50)
	R_2		37.90				1.078	
Metribuzin	D_2	56	–162.27	2.39	1.67	0.679	8.953	1.599 (50, 50)
	R_2		–2.77				8.677	
Dipropetryn	D_2	57	–249.91	2.39	1.67	0.679	4.698	1.599 (50, 50)
	R_2		37.22				13.289	
Cyromazine	D_2	37	–115.31	2.42	1.68	0.681	5.275	1.660 (40, 50)
	R_2		–16.22				3.888	
Simetryn	D_2	69	–397.44	2.67	1.67	0.679	13.309	1.599 (50, 50)
	R_2		95.81				4.778	
Trietazine	D_2	44	–136.82	2.70	1.68	0.681	28.593	1.660 (40, 50)
	R_2		14.49				9.853	
Terbutylazine	D_2	17	–42.86	2.90	1.74	0.689	15.543	2.077 (17, 50)
	R_2		21.43				4.973	
Terbutryn	D_2	39	–127.40	2.70	1.68	0.681	26.161	1.660 (40, 50)
	R_2		7.49				7.760	

[a][22].
[b]The data in brackets are the number of points of the first and the second regression straight lines respectively considered.
[c]*CL*=0.95

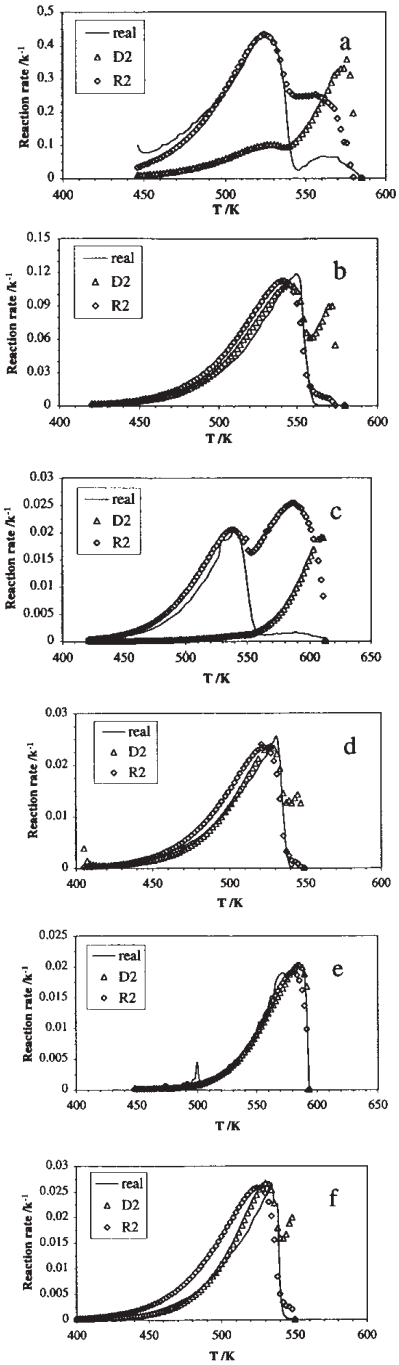

Fig. 3 Comparison between experimental and theoretical Arrhenius dα/dT curves for the 1,3,5-triazine derivatives studied symbolised according to Table 1

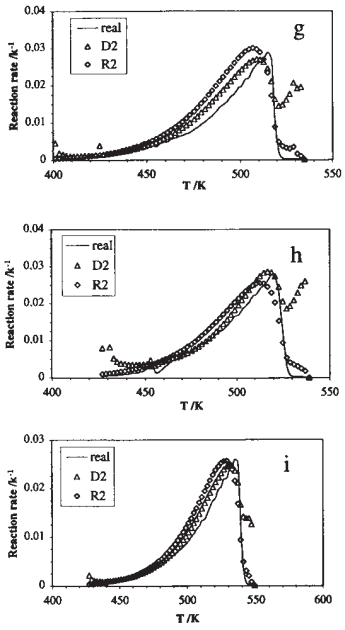

Fig. 3 Continued. Comparison between experimental and theoretical Arrhenius dα/dT curves for the 1,3,5-triazine derivatives studied symbolised according to Table 1

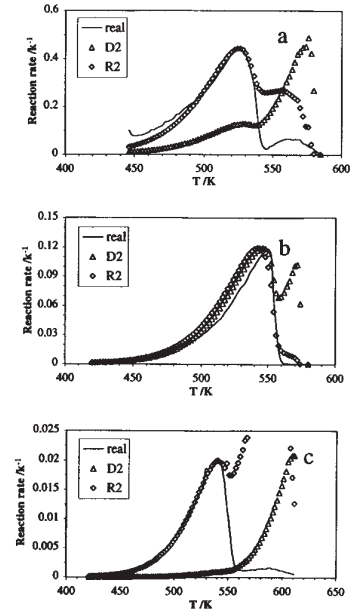

Fig. 4 Comparison between experimental and theoretical Satava dα/dT curves for the 1,3,5-triazine derivatives studied symbolised according to Table 1

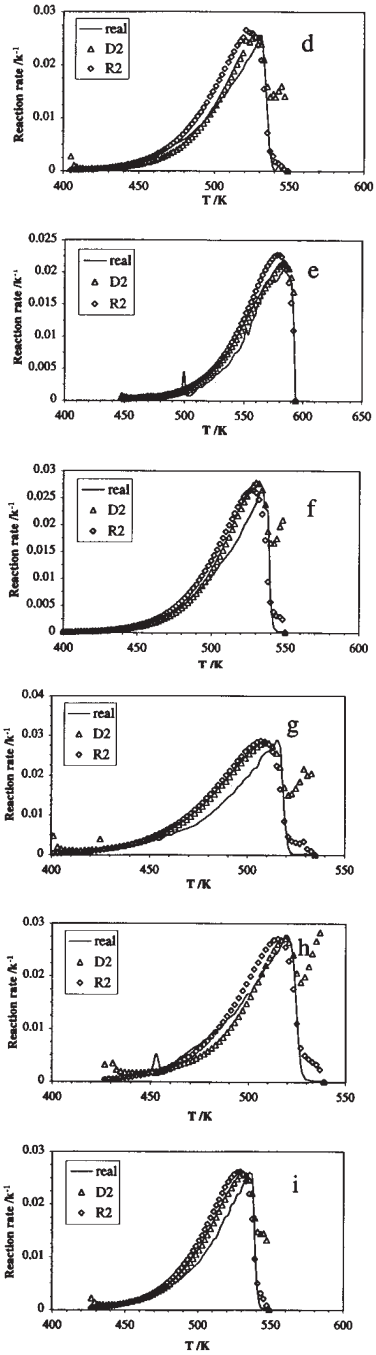

Fig. 4 Continued. Comparison between experimental and theoretical Satava dα/dT curves for the 1,3,5-triazine derivatives studied symbolised according to Table 1

Conclusions

The method used shows that all the compounds undergo vaporisation processes with diffusive (D_2) and geometrical model (contracting area R_2) processes.

Statistical analysis shows that the *E* and *A* parameters related to this method result to be more significant than those obtained by the method of calculation based on a first order mechanism (F_1) chosen a priori.

* * *

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