# KINETIC AND THERMODYNAMIC TREATMENT OF GASIFICATION PROCESS FOR SOME *s*-TRIAZINES

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## Abstract

Solid–gas phase transition processes of some triazines were studied from kinetic and thermodynamic viewpoint. DSC measurements and Clausius–Clapeyron equation were used to determine enthalpy values related to these processes. Model-fitting methods (based on Arrhenius, Šatava equations and Šesták–Berggren equations) and model-free methods (based on Ozawa–Flynn–Wall and Kissinger equations) allow to hypothesis R2 mechanism. An attempt to determine the activation parameters ($\Delta H^{\#}$, $\Delta G^{\#}$, $\Delta S^{\#}$) related to these processes was carried out. Accordance between the activation enthalpy values with those of activation energy obtained by means of kinetic methods and with the experimental (DSC) and calculated (Clausius–Clapeyron) enthalpy values was found.

**Keywords:** activation parameters, Clausius–Clapeyron equation, DSC, model-fitting, model-free, *s*-triazines

## Introduction

Pesticides have been the objects of numerous studies, based on various techniques. As these compounds are poorly solvated in water, they are usually present in the soil as solids [1]. Thus, the behaviour of pesticides in the solid phase gives very interesting information on their influence on the environment. This depends, in turn, on the soil features and on the number of factors such as wind, sunlight, rain and temperature [2–4]. Temperature affects the chemical degradation reactions of pesticides [5, 6], and thermal analysis can give important information on their thermal behaviour.

It is well known that thermal analysis of solid phases provides physical measurements of the thermal decomposition process for organic compounds but gives no chemical information about the studied process. The loss of chemicals from surfaces through the vapour phase is the main pathway for the loss of pesticides from agricultural land and that of other toxic organics from waste disposal sites [1] (e.g. in the case of fire). For this reason non-isothermal kinetic studies on the solid–gas phase transition processes that allow determining the probable mechanism and the kinetic

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parameters related to these processes (with or without decomposition process) are widely used.

This work was aimed to test the validity of the mechanisms for the above-cited processes related to some pesticides by means of kinetic parameters ($E_a$, $A$) obtained with various methods. These values were subsequently compared with the experimental (DSC curves) and calculated (Clausius–Clapeyron and Eyring equations) enthalpy values taking into account that for these processes the enthalpy is considered the lower limit of the activation energy.

An important class of pesticides, which can influence the environment, can be represented by the herbicides [7]. The most important compounds of this class are represented by the 1,3,5-triazines [8–11]. A large number of compounds based on this ring system have been synthetized and tested. Among them, the highly active triazines are characterized by having two substituted amino groups, with the third position usually being occupied by chloro-, alkoxy- and alkylthio-groups. Within the active series, small changes in the substitution pattern produce important differences in the biological activity. The compounds of this class used in the present work were: 2-chloro-4,6 bis-isopropyl amino-*s*-triazine, 2-chloro-4,6 bis (ethylamino)-*s*-triazine and 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine denoted as Propazine, Simazine and Atrazine, respectively. The molecular formulas, the structures and the molecular mass of these compounds are shown in Table 1.

Solid organic compounds submitted to heating treatment undergo liquid and gaseous phase transition with and without decomposition processes. From the thermodynamic standpoint, these transition phases are characterised by the enthalpy values while the kinetic aspect is recognised by means of the so-called kinetic triplet $E_a$, $A$ and $f(\alpha)$, where $f(\alpha)$ represents the reaction model as a function of the extent of conversion $\alpha$.
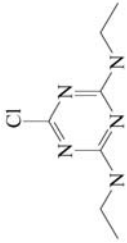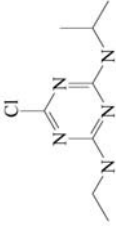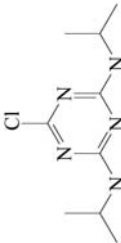
It was observed [12] that compounds with complex structures usually give rise to a thermal decomposition with various steps. Compounds with a simple structure usually do not undergo many steps pattern [13]. This behaviour is revealed by DSC curves where the presence of several exothermic and endothermic processes in a narrow range of temperature clearly indicates the complexity of the processes studied. However, some compounds with similar structures give rise to different thermodynamic values indicating that different processes occur. Kinetic analysis can be used to hypothesize the number and/or the types of mechanisms, which occur in the solid–gas phase transition processes using model-fitting and model-free methods of calculation.

Recently, many authors [14–21] have brought about a great improvement as regards kinetic analysis. Kinetic analysis of a decomposition process is traditionally expected to produce an adequate kinetic description of the process in terms of the reaction model and of the Arrhenius parameters using a single step kinetic equation

$$d\alpha/dt = k(T)f(\alpha) \qquad (1)$$

where $t$ is the time, $T$ is the temperature, $\alpha$ is the extent of conversion and $f(\alpha)$ is the reaction model. The temperature dependence of the rate constant is introduced by replacing $k(T)$ with the Arrhenius equation, which gives

**Table 1** Names, formulas and molecular masses $M_w$ of the *s*-triazines examined

| Compound | Name | Molecular formula | Structure | $M_w$ |
|---|---|---|---|---|
| Simazine | 2-chloro-4,6-bis(ethylamino)-*s*-triazine | $C_7H_{12}CiN_5$ |  | 201.5 |
| Atrazine | 2-chloro-4-(ethylamino)-6-(2-propylamino)-*s*-triazine | $C_8H_{14}CiN_5$ |  | 215.5 |
| Propazine | 2-chloro-4,6-bis(isopropylamino)-*s*-triazine | $C_9H_{16}ClN_5$ |  | 229.5 |

$$d\alpha/dt = A\exp(-E_a/RT)f(\alpha) \tag{2}$$

where $A$ (the pre-exponential factor) and $E_a$ (the activation energy) are the Arrhenius parameters and $R$ is the gas constant. For non-isothermal conditions $d\alpha/dt$ in Eq. (2) is replaced with $\beta d\alpha/dT$ where $\beta$ is the heating rate, giving

$$d\alpha/dT = (A/\beta)\exp(-E_a/RT)f(\alpha) \tag{3}$$

The three components ($f(\alpha)$, $E_a$ and $A$) define both in Eqs (2) and (3) a single-step reaction that disagrees with the multi-step nature of decomposition that usually occurs in the solid-state.

For compounds having complex structures it can be hypothesized that several steps with different activation energies will be involved in their decomposition processes. If a process involves several steps with different activation energies, the relative contributions of these steps to the overall reaction rate will vary with both the temperature and the extent of conversion. This means that the effective activation energy, determined from the analysis of the results, will also be a function of these two variables.

Following the model-fitting methods the $k(T)$ term is determined by the form of the $f(\alpha)$ chosen. In isothermal kinetics, these terms are separated by the conditions of the experiment ($k(T)$ is constant at constant temperature). The evaluation of the most suitable $f(\alpha)$ is achieved by fitting various reaction models to experimental data. After the $f(\alpha)$ term has been established for a series of temperatures, $k(T)$ can be evaluated. Single non-isothermal experiment provides information on both $k(T)$ and $f(\alpha)$ but not in separate form. For this reason, almost any $f(\alpha)$ can satisfactorily fit data by virtue of drastic variations in the Arrhenius parameters that compensate for the difference between the assumed form of $f(\alpha)$ and the true but unknown kinetic model [16].

In addition, for a simple step of decomposition process one cannot justifiably expect that identical values of Arrhenius parameters result from isothermal and non-isothermal experiments, which are necessarily conducted in different regions of temperature. However, the application of fitting models to isothermal parameters gives rise to more reliable values of Arrhenius parameters that, nevertheless, are likely to conceal the kinetic complexity [16]. Indeed, in the narrow ranges used under isothermal conditions, the differences between different models are much less visible and lead to a statistically acceptable description of the multi-step process by one set of kinetic parameters [16].

For this reason, the complex nature of a multi-step process can be more easily detected when using a broader temperature range in the non-isothermal method. An alternative approach to kinetic analysis is the model-free methods that allow for evaluating Arrhenius parameters without choosing the reaction model. The iso-conversional methods make up the best representation of the model-free approach. These methods yield the variation of the effective activation energy as a function of the extent of conversion [16]. The knowledge of the dependence of $E_a$ on $\alpha$ allows detecting multi-step processes and predicting some mechanistic conclusions on the reaction kinetics over a wide temperature range.

Another possibility to determine the kinetic parameters of simple and complex decomposition processes is represented by the direct non-linear regression and to propose a method for their calculation from a single TG curve [13]. The usual 'single curve' methods are based on a linearization of the fundamental kinetic equations. They are relatively satisfactory for simple processes where their results are often comparable with those obtained by the reliable isoconversional methods [13]. However, if a TG curve consists of two or more overlapping processes, the 'single curve' methods fail. The reason of the failure is the kinetic equation linearization which may be performed in the curve section where only a single process proceeds.

Recent expansion and development of computers provides iterative methods that utilise the direct non-linear regression applied to the $\alpha$–$T$ plots. The limitation for the calculation of the kinetic parameters can be reduced by the use of a direct non-linear regression. The use of non-linear regression as a method of determining the kinetic parameters of heterogeneous reactions from single TG curves [22] supports the justifiability of this approach.

## Experimental

The experimental measurements were carried out on a Stanton Redcroft 625 simultaneous TG-DSC connected to a 386 IBM-compatible personal computer. Calibration of this instrument was performed with standard indium, lead, tin, zinc, naphthalene and benzoic acid samples of known temperatures and enthalpies of melting. The metals possess over 99.99% purity and the organic compounds over 99.95%. The chlorinated pesticides (Polyscience) were used without purification and their purity (99%) was more than that required for the application of DSC [23, 24]. Their purity was checked by gas chromatographic-mass spectrometry measurements. Their common names, molecular formulas, structures and molecular masses are shown in Table 1.

To carry out solid–gas phase transition process studies under rising temperature conditions, the TG-DSC apparatus was set up as follows. Samples (8–10 mg) were weighed in aluminium pans placed in an argon-filled dry box. The TG-DSC system was flushed with argon gas below (at flow rate of 50 mL min$^{-1}$) and above (at flow rate of 30 mL min$^{-1}$) the open pans. In this way the gas evolved during the thermal solid–gas phase process was removed continuously. The heating rates used were 2.5, 5, 10, 15 and 20 K min$^{-1}$ and at least three runs were made for each compound. All the thermodynamic quantities were calculated using the Stanton–Redcroft data acquisition system, Trace 2, Version 4.

The gaseous products of thermal processes were adsorbed into suitable adsorbent (Supelco) tubes: Chromosorb, glass fiber filter, coconut charcoal and activated silica gel. Subsequently these tubes were desorbed into an organic liquid ($CS_2$) and injected into a 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 $\mu$m (Supelco). The GC oven was held at 343.15 K for 2 min, then it was scanned at 2.5 K min$^{-1}$ to 553.15 K. Carrier gas (helium) flow was 0.8 mL min$^{-1}$. Mass Spectrometry (MS) determinations were per-

formed with the SCAN technique using electron impact ionization at 70 eV and the transfer line was maintained at 553.15 K.

*Procedure*

Thermodynamics

TG/DSC measurements mainly aim at stressing the evaluation of extrapolated onset temperatures, the mass loss percentage and the enthalpy values of any process occurring at rising temperature (melting, crystallization, polymorphic changes, decomposition, chemical reactions). During heating all the compounds undergo sublimation followed by melting and evaporation processes.

The thermodynamics of the processes regarding the compounds, which exhibit a liquid-gas phase transition (without decomposition), can be examined assuming that the system attains equilibrium at any stage. When the equilibrium is achieved, the extent of the mass loss at a given temperature, $\alpha$, can be described by the ratio of the equilibrium vapour pressure $P$ to the atmospheric pressure $P^0$ for dynamic experiment carried out at low heating rates (2.5 K min$^{-1}$) in static air.

The volatilization process can be described by the integral of the Clausius–Clapeyron equation:

$$\ln \frac{P}{P^0} = \ln \alpha = \frac{\Delta H_V}{R} \frac{1}{T_V} - \frac{\Delta H_V}{R} \frac{1}{T} \tag{4}$$

where $T_V$ and $\Delta H_V$ are related to the vaporization processes and $P^0$ to the boiling temperature. Substituting $P/P^0$ with the experimental $\alpha$ values and plotting $\ln \alpha$ *vs*. $1/T$ one can determine $\Delta H_V$ and $T_V$ and compare them with those obtained by TG/DSC curves to point out if only vaporization process occurs. This equation has been applied to the studied processes and the obtained enthalpy values were compared with those of the DSC curves which allow to calculate the sum of the enthalpy values related to sublimation and evaporation processes. A good accordance between the $\Delta H$ values allows confirming the used procedure.

Non-isothermal methods

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 [25–28] developed a computer program that plots theoretical $d\alpha/dT$ curve by using the Eq. (3) when a hypothesized mechanism $f(\alpha)$ and suitable values of both $A$ and $E_a$ are introduced. This approach may be considered as the reverse of the Arrhenius non-isothermal kinetics in which $A$ and $E_a$ are calculated both from the $\alpha–T$ plots and a proper mechanism function $f(\alpha)$. The shape of the theoretical curve obtained in this way, results to be only a function of the mechanism and allows determining it by considering the following parameters: *i*) initial ($T_i$) and

final ($T_f$) temperature of 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 and *iii*) the value of $\alpha_{max}$ at the maximum rate of the process (at $T_p$) in the $\alpha$–*T* plot.

The comparison of these characteristic quantities (half width, $\alpha_{max}$, $T_i$ and $T_f$) for experimental curves with those reported in literature 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 $E_a$ the following method can be used.

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

$$\ln[(\beta d\alpha/dT)/f(\alpha)]=\ln k=\ln A-E_a/RT \tag{5}$$

The $\alpha$ values are also inserted in the mathematical integral expression $g(\alpha)$ and used, together with $\beta$ in the Šatava integral equation

$$\log[g(\alpha)]=-0.4567(E_a/RT)-2.3115+\log(AE_a/R\beta) \tag{6}$$

where Doyle's approximation is valid in a temperature range of 100 K [29].

The Arrhenius parameters can be calculated by means of the following two linear relationships

$$\ln[(\beta d\alpha/dT)/f(\alpha)] \textit{ vs. } 1/T \tag{7}$$

$$\log[g(\alpha)] \textit{ vs. } 1/T. \tag{8}$$

From the coefficient and the intercept of the regressions straight lines, the $E_a$ and *A* parameters can be calculated. Finally, the values of *A* and $E_a$ and the related mechanisms represented by $f(\alpha)$ were inserted in Eq. (3) and the theoretical DTG curves are reconstructed and compared to the experimental ones. Values of triplets obtained in this way can be used in non-isothermal model-fitting method.

To obtain the $E_a$ values related to non-isothermal isoconversional method the Ozawa–Flynn–Wall equation

$$\log\beta = -0.4567(E_a/RT)-2.3115+\log(AE_a/R)-\log[g(\alpha)] \tag{9}$$

was applied to non-isothermal TG curves.

Kissinger [30, 31] and other authors [32, 33] have found that the peak temperature is a function of the heating rate of the sample through the following (pseudo) first-order reaction

$$\ln(\beta/T_p^2)=\ln(AR/E_a)-E_a/RT_p \tag{10}$$

where $\beta$ is the heating rate, $T_p$ the peak temperature and *R* the gas constant. This equation can be applied with a reasonable approximation even to an $n^{th}$-order, regardless order. If the reaction proceeds under conditions where thermal equilibrium is always maintained, then a plot $\ln(\beta/T_p^2)$ *vs.* $1/T_p$ gives a straight line with a slope equal to $-E_a/R$.

*Non-linear regression*

The majority of the models represented by $f(\alpha)$ functions can be accommodated in modifications of the Šesták–Berggren equation,

$$f(\alpha)=(\alpha)^m(1-\alpha)^n[-\ln(1-\alpha)]^p$$

which, applied to Eq. (3), has the general form

$$d\alpha/dT=(A/\beta)\exp(-E_a/RT)(\alpha)^m(1-\alpha)^n[-\ln(1-\alpha)]^p \qquad (11)$$

where *m*, *n* and *p* are constants. Proper values of *m*, *n* and *p* related to different kinetic models are reported in Table 2.

**Table 2** Constant values of Šesták–Berggren equation for each model function

| Model | *m* | *n* | *p* |
|---|---|---|---|
| R2 | 0 | 1/2 | 0 |
| R3 | 0 | 2/3 | 0 |
| F0 | 0 | 0 | 0 |
| F1 | 0 | 1 | 0 |
| F2 | 0 | 2 | 0 |
| D1 | −1 | 0 | 0 |
| D2 | 0 | 0 | −1 |

To calculate a theoretical $\alpha$–$T$ plot (the reversal of a TG curve), it is necessary to know the form of the function $\alpha=f(T, E_a, A)$. If the temperature set is set small enough (i.e. 0.5 K), the derivatives in Eq. (11) may be replaced by differences. We assume that the $\alpha$–$T$ plot is composed of very small linear segments of the length $\Delta T$, in which the reaction rate $d\alpha/dT$ is constant.

$$\Delta\alpha=(A/\beta)\exp(-E_a/RT)f(\alpha)\Delta T \qquad (12)$$

Assuming the $\alpha_0$ close to zero (i.e. $10^{-4}$) and $T_0$ at the beginning of the decomposition step in the TG curve, further points of the theoretical $\alpha$–$T$ plot can be calculated from the following relations

$$\alpha_i=\alpha_{i-1}+(A/\beta)\exp(-E_a/RT_{i-1})f(\alpha)(T_i-T_{i-1}) \qquad (13)$$

Searching for these parameters is a typical regression problem, where Eq. (13) is non-linear in relation to the searched parameters. To this end, an iterative method was employed. Then, $\alpha(i)$ was calculated and compared to the corresponding experimental value: then, the sum of their squared differences was minimised by varying $\ln A$ and $E_a$. Obtained values were used to calculate $\alpha(i+1)$ by means of Eq. (13): this value was compared with the corresponding experimental one and a new set of $\ln A$ and $E_a$ values were obtained after minimization.

The iterative procedure can be summarised as follows:

1. set $m$, $n$, $p$ values (choice of model)
2. set $\alpha_0 = \alpha_{calc}(0) = 0.0001$
3. calculate $\alpha_{calc}(i) = \alpha_{calc}(i-1) + (A/\beta)\exp(-E_a/RT_{i-1})f(\alpha)(T_i - T_{i-1})$
4. calculate $S = \sum\limits_{j=0}^{i}(\alpha_{calc}(j) - \alpha_{sper}(j))^2$
5. minimize $S$ by varying $\ln A$ and $E_a$
6. back to point 3 restarting with $\alpha_{calc}(i+1)$

After this iterative step-by-step method, calculated $\alpha$ values fit experimental ones: as a consequence, $\ln A$ and $E_a$ best-fitting values for the chosen mechanism ($f(\alpha)$) were obtained.

Reliability of the obtained results were evaluated by a simple test of significance based on $F$ parameter:

$$F_{calc} = (\sigma_{calc}/\sigma_{exp})^2$$

where $\sigma_{calc}$ is the standard deviation of theoretical model, calculated using the sum of squared differences ($\alpha_{calc} - \alpha_{sper}$) while $\sigma_{exp}$ can be set as the instrumental error of the measurement [34].

Activation parameters

Two basic processes as chemical reaction and diffusion always contribute in the heterogeneous reactions.

The concept of chemical reaction denotes chemical interaction of one or more components from an initial (reactants) to a final stage (products). The mathematical description of these processes is based on the reaction order. One of the most productive theories in modern chemical kinetics is the activated complex theory [35–37]. This theory assumes a certain reaction intermediate state $A^{\#}$, to which certain values of thermodynamic functions can be ascribed. The rate of the process is determined by the rate of the decomposition of complex $A^{\#}$ to the final products. From a theoretical point of view, the rate of the given process can be expressed as $[(k_BT)/h]K^{\#}$ [38], where $k_B$ and $h$ are the Boltzmann and Plank constants, while $K^{\#}$ has the significance of an equilibrium constant that characterizes the equilibrium between the activated complex and the reactants. On substitution for $K^{\#}$

$$k(T) = [(k_BT)/h]\exp(-\Delta G^{\#}/RT) = [(k_BT)/h]\exp(-\Delta H^{\#}/RT)\exp(-\Delta S^{\#}/R) \qquad (14)$$

where $\Delta G^{\#}$, $\Delta S^{\#}$ and $\Delta H^{\#}$ are the Gibbs energy, entropy and enthalpy for the activated complex formation from the reactants, respectively.

A decomposition reaction is defined as a process in which a chemical is degraded into simpler species. Such reactions may include processes in which the crystal lattice structure is destroyed, such a melting, evaporation, sublimation, as well as chemical reactions that resulting the formation of a new compound [39]. In all solid-state decompositions, the transformations occur in an area of enhanced activity,

referred as to reaction interface or the boundary between the reactant and the product [39]. For these chemical reactions [38], Eq. (14) can be applied to search a relationship between a thermodynamic (or statistical) description of the given process and the magnitude of the activation energy values.

Some $E_a$ values were correlated with the enthalpy values for some solid decomposition processes and the difference within these values is often negligible but is large when compared with similar values for homogeneous reactions [38]. This fact allows to hypothesize that Arrhenius equation cannot be applied to solid-state decomposition processes and to doubt the validity of the activated complex concept [38]. Anyway, solid–gas phase transition processes can be considered as a special case of activated complex theory, which describes the intermediate state with the highest energy on the reaction pathway.

By considering the equivalent expression for rate constant represented by Arrhenius equation

$$k(T)=A\exp(-E_a/RT) \tag{15}$$

the frequency factor $A$ can be express as

$$A=[(k_B T)/h]\exp(-\Delta S^{\#}/R) \tag{16}$$

From Eq. (16) it is evident that A values are greatly influenced by $\Delta S^{\#}$ values. Moreover, by comparing Eqs (14)–(16) it may be concluded that activation energy values obtained from Eq. (15) have to be considered as molar enthalpies of activation.

## Results and discussion

### *Features of the thermal processes*

By comparison of TG/DSC curves for the three compounds (Fig. 1, Table 3) it can be seen that there are two endothermic processes representing sublimation, melting and evaporation processes.

For the three examined compounds the melting process appears after the beginning of the sublimation and the evaporation processes. This behaviour is evident from the superimposition of the two endothermic effects in the DSC curves. By virtue of this fact, the sum of the enthalpy of sublimation and evaporation processes is obtained by subtracting the enthalpy of melting from the overall enthalpy of the three processes. The extrapolated temperatures and $\Delta H$ values calculated by linearizing Eq. (4) are in agreement with those calculated by DSC measurements (Table 3). This means that enthalpy values obtained from Clausius–Clapeyron equation can be considered as the sum of both sublimation and evaporation processes. Moreover, in the case of Atrazine the melting and the vaporization processes (DSC curve in Fig. 1a) are more easily distinguished with respect to what happens in the case of Propazine and Simazine (DSC curves in Fig. 1b and 1c). This entails a better agreement between enthalpies obtained by DSC curves and those calculated by Eq. (4) for Atrazine (Fig. 2 and Table 3).
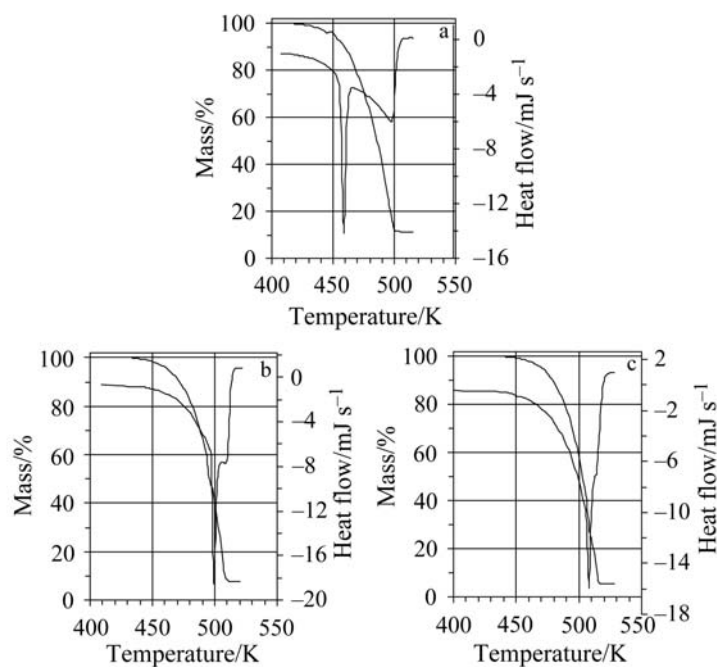
**Fig. 1** Simultaneous TG/DSC curves in air at 5 K min$^{-1}$ of a – Atrazine; b – Propazine and c –Simazine
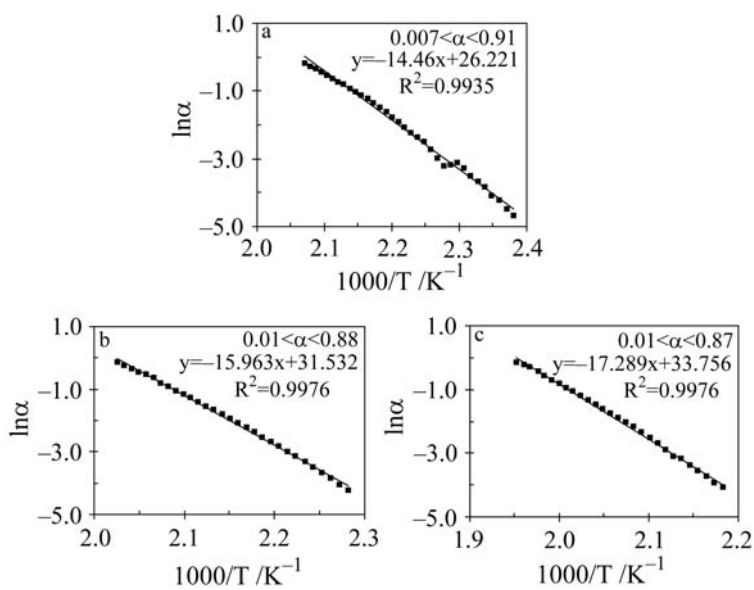


**Fig. 2** Plot of ln α *vs.* 1/*T* for a – Simazine; b – Atrazine and c – Propazine

**Table 3** Extrapolated onset and peak temperatures ($T_e$ and $T_p$, respectively), enthalpy changes and mass loss percentage obtained from dynamic TG and DSC measurements ($\beta$=5 K min$^{-1}$) for the thermal processes of the *s*-triazine studied. Enthalpy values of melting collected from literature [24] are reported in brackets

| Compounds | Temperature values/K | | | | | | $\Delta H$ values/kJ mol$^{-1}$ | | | Mass loss/% |
|---|---|---|---|---|---|---|---|---|---|---|
| | from TG[a] | from DSC | | | | from[c] | from DSC | | from[c] | |
| | | melting[a] | melting[b] | vaporization[a] | vaporization[b] | | melting | vaporization | | |
| Simazine | 479.6 | 504.2 | 508.4 | 496.2 | N.D. | 512.2 | 25.0 (43.9) | 133.6 | 143.7 | 94.8 |
| Atrazine | 472.0 | 452.7 | 454.2 | 441.3 | 497.1 | 494.8 | 31.6 (40.6) | 122.7 | 120.2 | 88.6 |
| Propazine | 471.8 | 493.6 | 496.3 | 464.0 | 506.1 | 506.2 | 22.2 (41.8) | 141.2 | 132.7 | 92.2 |

[a]Extrapoled temperatures values.
[b]Peak temperatures values.
[c]Calculated using the Clausius–Clapeyron equation.
[d]N.D.=no detectable.

*GC-MS measurements*

The total ion current chromatograms (TICs) and 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 with very good match quality of the spectra. For the sake of shortness the corresponding spectra are not reported herein.

*Non isothermal kinetics*

Model-fitting, model-free and non-linear regression methods

The Dollimore computer program used in non-isothermal method [25–28] can be applied to our experimental curves for the group of pesticides considered. It is shown that $\alpha_{max}$ is characteristic of some specific mechanism and practically does not depend on the Arrhenius parameters and on the heating rate $\beta$. 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 vaporization taken from TG/DSC curves are reported in Table 4.

**Table 4** Parameters related to mechanism-characteristic features for thermal processes of the studied *s*-triazines obtained from TG/DTG curves according to [27]

| Compound | From TG curves | | From DTG curves | | | | Kinetic models |
|---|---|---|---|---|---|---|---|
| | Characteristic features of $T_i$ and $T_f$ | $\alpha_{max}$ | $T_i$/K | $T_f$/K | $\dfrac{\Delta T_{lo}}{\Delta T_{hi}}$ | Half width/ K | |
| Simazine | $T_i$ diffuse $T_f$ sharp | 0.87 | 467.2 | 506.3 | 1.2 | 14.8 | D2, R2 |
| Atrazine | $T_i$ diffuse $T_f$ sharp | 0.90 | 447.5 | 497.1 | 5.8 | 13.6 | D2, R2 |
| Propazine | $T_i$ diffuse $T_f$ sharp | 0.88 | 461.1 | 506.0 | 3.6 | 12.7 | D2, R2 |

All the compounds examined show the same typical TG/DTG shapes: *i*) TG curves with a diffuse initial or onset temperature and a sharp final one; *ii*) DTG curves with a ratio $\Delta T_{lo}/\Delta T_{hi}$ (which represents the asymmetry of the DTG curves) always greater than the unity.

By comparing our experimental $\alpha_{max}$ and half width values with the theoretical ones reported in the literature by Dollimore and co-workers [25–28], one can hypothesizes D2 and R2 as the most suitable mechanisms. A differential and an integral model-fitting methods based on Eqs (5) and (6), respectively, were applied and the kinetic parameters obtained are summarized in Table 5. A further confirmation that D2 and R2 seem to be the most suitable mechanisms is due to the comparison of the corresponding values for $r^2$.

**Table 5** Kinetic parameters extrapoled from linearization of Arrhenius and Šatava equations related to the thermal processes for the *s*-triazines examined

| Compound | Model | Arrhenius equation | | | Šatava equation | | |
|---|---|---|---|---|---|---|---|
| | | $E_a$/kJ mol$^{-1}$ | ln$A$/s$^{-1}$ | $r^2$ | $E_a$/kJ mol$^{-1}$ | ln$A$/s$^{-1}$ | $r^2$ |
| Simazine | D1 | 280.2 | 70.1 | 0.9954 | 268.0 | 74.3 | 0.9959 |
| | D2 | 295.2 | 73.3 | 0.9976 | 284.0 | 77.9 | 0.9991 |
| | R2 | 140.1 | 36.0 | 0.9943 | 145.0 | 44.2 | 0.9993 |
| | R3 | 142.9 | 36.4 | 0.9899 | 182.1 | 56.0 | 0.9575 |
| | F0 | 131.7 | 34.5 | 0.9894 | 145.9 | 45.1 | 0.9948 |
| | F1 | 148.5 | 38.9 | 0.8242 | 153.7 | 47.2 | 0.9977 |
| | F2 | 165.4 | 43.3 | 0.9420 | 149.7 | 45.4 | 0.9972 |
| Atrazine | D1 | 231.4 | 57.7 | 0.9957 | 236.4 | 68.9 | 0.9898 |
| | D2 | 236.5 | 61.1 | 0.9845 | 244.8 | 70.6 | 0.9845 |
| | R2 | 113.8 | 30.6 | 0.9686 | 122.1 | 39.8 | 0.9966 |
| | R3 | 109.1 | 29.1 | 0.9548 | 147.2 | 48.7 | 0.8966 |
| | F0 | 96.4 | 26.7 | 0.8939 | 117.7 | 40.9 | 0.9908 |
| | F1 | 115.1 | 31.9 | 0.1021 | 126.4 | 41.7 | 0.9964 |
| | F2 | 134.7 | 37.1 | 0.9466 | 122.0 | 39.8 | 0.9960 |
| Propazine | D1 | 202.3 | 51.9 | 0.9959 | 189.2 | 55.6 | 0.9958 |
| | D2 | 215.9 | 54.8 | 0.9927 | 201.4 | 58.3 | 0.9907 |
| | R2 | 121.6 | 31.8 | 0.9973 | 114.8 | 37.3 | 0.9947 |
| | R3 | 128.8 | 33.3 | 0.9857 | 163.1 | 51.6 | 0.9504 |
| | F0 | 114.8 | 30.7 | 0.9900 | 86.6 | 30.7 | 0.9876 |
| | F1 | 135.8 | 36.6 | 0.6220 | 96.1 | 33.3 | 0.9677 |
| | F2 | 156.9 | 41.9 | 0.9440 | 91.2 | 31.3 | 0.9795 |

The change in $E_a$ obtained by non-isothermal isoconversional method using Eq. (9) is reported in Table 6 and Fig. 3 while the results obtained by Kissinger equation are given in Table 7. Table 8 shows the $E_a$ and the ln$A$ values obtained using non-linear regression.

By considering the *F* values calculated as the square of the ratio $\sigma_{calc}/\sigma_{exp}$ since the lower is the *F* value the more reliable is the chosen model, it can be concluded that R2 mechanism is the best one at least for Atrazine and Simazine. Anyway, the trends of $E_a$ and the ln$A$ obtained according to this mechanism are in good agreement with those calculated from linearization of Arrhenius equation (Table 4). Also, the values of $E_a$ and the ln$A$ agree satisfactorily. Previous results described above suggest narrowing the number of kinetic models to be examined. Therefore, the enthalpy values related to solid–gas phase transition processes calculated by using Eq. (14) according to the most appropriate models are given in Table 8 and Fig. 4. For the three compounds there is good accordance for the activation energy values obtained with various methods and a mechanism R2 can be hypothesized for them. Moreover, for Simazine, for which the sublimation process is prevailing, enthalpy values obtained by DSC and Clausius–Clapeyron equation agree with the activation energy values calculated using Šesták–Berggren (R2), Arrhenius (R2) equations and with the enthalpy values calculated by means of Eq. (14). For Propazine there is good accordance among the activation energy values calculated using Arrhenius (R2),

Šesták–Berggren (R2) and the enthalpy value of Eq. (14) according to a R2 mecha-
nism. For Atrazine enthalpy values obtained from DSC measurements and the
Clausius–Clapeyron equation are close and agree with the $E_a$ values calculated by
Šatava (R2) and Kissinger equations.

**Table 6** Activation energy values (kJ mol$^{-1}$) obtained according to Ozawa–Flynn–Wall
model-free kinetic method for the *s*-triazines studied

| α | Simazine | Atrazine | Propazine |
|---|---|---|---|
| 0.05 | 113.8 | 111.5 | 133.4 |
| 0.10 | 113.1 | 110.9 | 131.7 |
| 0.15 | 113.6 | 111.0 | 131.6 |
| 0.20 | 113.1 | 110.7 | 130.5 |
| 0.25 | 113.7 | 111.7 | 131.2 |
| 0.30 | 113.8 | 112.0 | 133.0 |
| 0.35 | 114.8 | 113.1 | 131.5 |
| 0.40 | 116.0 | 114.1 | 131.8 |
| 0.45 | 117.0 | 114.9 | 132.8 |
| 0.50 | 118.1 | 115.5 | 133.8 |
| 0.55 | 119.3 | 116.1 | 133.7 |
| 0.60 | 120.2 | 117.0 | 135.7 |
| 0.65 | 121.0 | 117.6 | 135.9 |
| 0.70 | 120.8 | 117.7 | 136.7 |
| 0.75 | 121.6 | 117.9 | 137.4 |
| 0.80 | 121.8 | 118.4 | 138.0 |
| 0.85 | 122.2 | 119.9 | 137.0 |
| 0.90 | 121.5 | 119.8 | 137.9 |
| 0.95 | 120.5 | 119.2 | 138.6 |
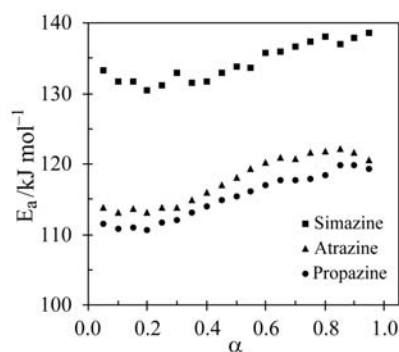


**Fig. 3** Activation energies (kJ mol$^{-1}$) as a function of the degree of conversion α as ob-
tained from dynamic model-free method for the triazines studied

**Table 7** Activation energy values (kJ mol$^{-1}$) obtained from Eq. (10) for the *s*-triazines studied

| Compounds | $E_a$ |
|-----------|-------|
| Simazine | 144.0 |
| Atrazine | 127.8 |
| Propazine | 126.0 |

**Table 8** Kinetic parameters of activation obtained from non-linear regression applied to Šesták–Berggren equation for the most suitable reaction models

| Compounds | Model | Kinetic parameters | | Statistical parameters[*] | | |
|-----------|-------|-------------------|------------|--------|--------------|-----------|
| | | $E_a$/kJ mol$^{-1}$ | ln$A$/min$^{-1}$ | $r^2$ | $\sigma_{cal}$ | $F_{cal}$ |
| Simazine | R2 | 136.1 | 31.1 | 0.9995 | 0.0143 | 2.0312 |
| | R3 | 137.8 | 31.5 | 0.9983 | 0.0274 | 7.5051 |
| | F0 | 125.2 | 28.2 | 0.9971 | 0.0184 | 3.3886 |
| | F1 | 155.5 | 36.0 | 0.9972 | 0.0292 | 8.5006 |
| | F2 | 257.6 | 61.5 | 0.9912 | 0.0413 | 17.0415 |
| | D1 | 274.0 | 63.1 | 0.9919 | 0.0236 | 5.5685 |
| | D2 | 291.4 | 67.6 | 0.9975 | 0.0146 | 2.1227 |
| Atrazine | R2 | 108.6 | 25.3 | 0.9994 | 0.0085 | 0.7217 |
| | R3 | 113.8 | 26.7 | 0.9990 | 0.0134 | 1.7998 |
| | F0 | 88.3 | 19.9 | 0.9975 | 0.0145 | 2.0885 |
| | F1 | 130.0 | 31.0 | 0.9980 | 0.0200 | 3.9813 |
| | F2 | 200.3 | 49.4 | 0.9909 | 0.0413 | 17.0370 |
| | D1 | 216.0 | 51.0 | 0.9870 | 0.0310 | 9.6398 |
| | D2 | 231.6 | 55.2 | 0.9954 | 0.0188 | 3.5350 |
| Propazine | R2 | 123.7 | 28.4 | 0.9986 | 0.0232 | 5.3967 |
| | R3 | 126.0 | 29.0 | 0.9967 | 0.0346 | 11.9547 |
| | F0 | 114.3 | 25.9 | 0.9987 | 0.0110 | 1.2145 |
| | F1 | 149.6 | 35.1 | 0.9966 | 0.0283 | 7.9954 |
| | F2 | 240.5 | 58.2 | 0.9884 | 0.0452 | 20.4535 |
| | D1 | 251.6 | 58.5 | 0.9946 | 0.0191 | 3.6638 |
| | D2 | 278.0 | 65.3 | 0.9984 | 0.0146 | 2.1192 |

[*]Experimental standard deviation was 0.01 for all calculations.

The thermal processes for the three studied compounds follow R2 mechanisms. According to Dollimore [40, 41] it can be affirmed that mechanisms such as F1, R1 and R2 other than zero-order can describe, over a small change in temperature, the solid–gas transition processes examined.

Although Eq. (14) cannot be always applied to reaction of this type, the accordance among the values of activation enthalpy $\Delta H^{\#}$, activation energy $E_a$ (both of them according to a R2 mechanism) and those obtained from DSC curves and extrapolated from Clausius–Clapeyron equation, seems to be not a coincidence. Moreover, it can be observed that the processes are equally hindered by free-energy values, while the entropy value is negative for Atrazine and Propazine and positive for Simazine. This result indi-
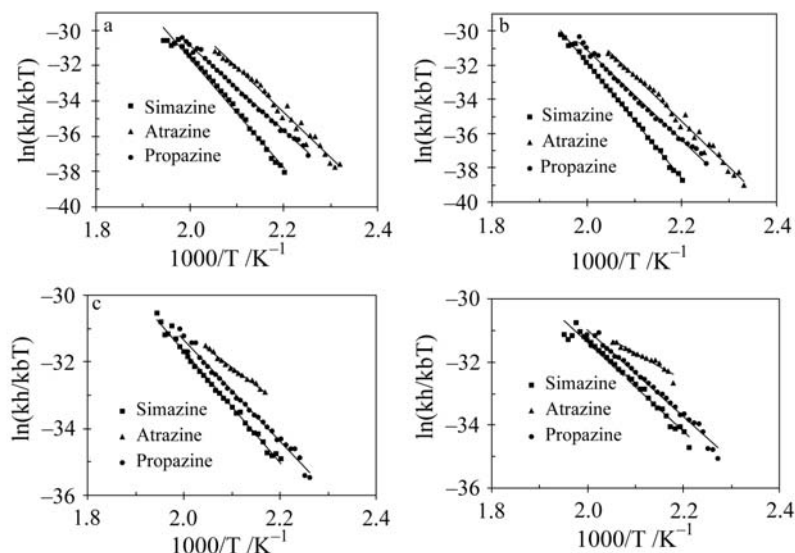
**Fig. 4** Plot of ln($kh/k_BT$) *vs.* $1/T$ according to a – D1; b – D2; c – R2 and d – FO mechanisms for the triazines studied
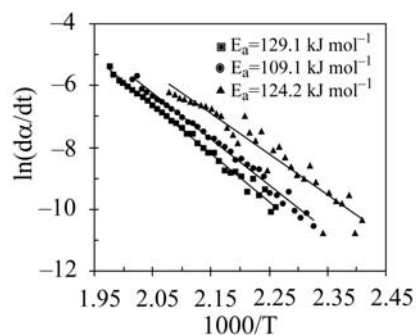


**Fig. 5** Plot of lnd$\alpha$/d$t$ *vs.* $1/T$ for ■ – Simazine; ● – Atrazine and ▲ – Propazine

cates that, Atrazine and Propazine undergo solid–gas phase transitions with a decrease in the degree of freedom for vibrational mode while for Simazine the contrary is true.

Finally, the *A* values calculated from the experimental results ($10^{13}$ s$^{-1}$) were in agreement within a factor ranging from 1 to $10^2$ with the vibrational frequency of a crystal constituent at a surface or interface. This agreement has to be expected from the Polany–Wigner equation [42–45] even if this equation has been criticised [46].

## Conclusions

Model-fitting and model-free kinetic methods together with experimental measurements were used to describe solid–gas phase transition processes of some pesticides. In spite of the fact that superimposed reactions make difficult to read the DSC curves,

there is good accordance between thermodynamic and kinetic parameters related to these processes.

In particular, as far as concerns Atrazine, it can be observed that the enthalpy values obtained from DSC and those calculated by Eq. (4) are in good agreement with each other (Table 3). Moreover, the above-mentioned enthalpy values agree satisfactorily with the $E_a$ values obtained from the different kinetic methods used (being R2 of the Šatava method and that of Kissinger equation the better ones).

These evidences demonstrate that the thermodynamic and the kinetic approaches reported in this research enable the examined processes to be well described also with respect to the hypothesis of a possible mechanism.

<center>*   *   *</center>

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