

**Comments on “Thermal decomposition of pyridoxine: an evolved gas analysis-ion attachment mass spectrometry study”. About the application of model-fitting methods of kinetic analysis to single non-isothermal curves.**

**Pedro E. Sánchez-Jiménez\***, Luis A. Pérez-Maqueda, Antonio Perejón, José M. Criado

*Instituto de Ciencia de Materiales de Sevilla, C.S.I.C.-Universidad de Sevilla, C. Américo Vesputio n°49, 41092 Sevilla, Spain*

**RATIONALE:** This reply reports a significant flaw in the kinetic analysis presented in a paper recently published in Rapid Communications in Mass Spectrometry journal, which consists in the application of model-fitting methods of kinetic analysis to a single non-isothermal experimental curve.

**METHODS:** A model-fitting method of kinetic analysis is applied to data simulated using a Runge-Kutta 4<sup>th</sup> order numerical integration method by means of the Mathcad software.

**RESULTS:** Here, it is shown that model-fitting methods of kinetic analysis cannot be applied to single non-isothermal experimental curves because a good fit to the experimental data is obtained regardless the kinetic model assumed.

**CONCLUSIONS:** Evolved gas analysis-Li<sup>+</sup> ion attachment mass spectrometry (EGA-Li<sup>+</sup>IAMS) can be of tremendous interest towards obtaining data usable for performing kinetic studies. However, the determination of the activation energy and the discrimination of the kinetic model are not possible unless more than one experimental curve is used.

Dear Editor,

In a paper recently published in Rapid Communications in Mass Spectrometry, the thermal decomposition of pyridoxine was studied by means of the evolved gas analysis-Li<sup>+</sup> ion attachment mass spectrometry (EGA-Li<sup>+</sup>IAMS) technique.<sup>[1]</sup> This is a technique that presents a great potential for the kinetic study of thermal decomposition reactions. In such paper, the decomposition products were identified and, additionally, a kinetic analysis of the process was carried out. For that purpose, Juhasz *et al* used the total ion monitoring (TIM) curve, which indicates the amount of products released at any given time and, consequently, it can be related to the rate of reaction as a function of time or temperature. Then, the extent of conversion at a certain time or temperature was determined by integrating the area under the TIM curve from the beginning of the signal until the selected

---

\*Corresponding author. Tel +34954489548 Fax +34954460665  
e-mail address: pedro.enrique@icmse.csic.es

time/temperature.<sup>[1]</sup> With that information, the kinetic parameters driving the reaction; i.e, the activation energy and preexponential factor, were calculated by fitting the experimental data extracted from the TIM curve to a first order kinetic model. At a first glance, it is a standard model-fitting method of kinetic analysis but, as employed, it entails two significant flaws that we aim to clarify here: performing the analysis with data from a single non-isothermal experimental run, and fitting the data to a first order model, without testing other possible models.

It is well known that a reaction is kinetically described by three parameters, the activation energy, the preexponential factor and the kinetic model. They constitute the so called kinetic triplet. The kinetic model is an algebraic function that reflects the relationship between reaction rate and conversion and it can be related to a reaction mechanism. During the last decades a number of theoretical kinetic models have been proposed.<sup>[2-4]</sup> Model-fitting methods of kinetic analysis are widely used because of their simplicity and basically consist in fitting the experimental data to several of such kinetic models. The model providing the best fit is usually regarded as the correct one, and the activation energy is deduced from the slope of the fit. Unfortunately, it has been long established that the kinetic parameters cannot be reliably determined from a single non isothermal curve because the experimental data provide a reasonable fit regardless of the kinetic model employed.<sup>[5-8]</sup> As an example, Figure 1 includes a simulated  $\alpha$ -T curve, constructed using the following kinetic parameters:  $E_a=100 \text{ kJ mol}^{-1}$ ,  $A=10^{10} \text{ s}^{-1}$  and an Avrami-Erofeev A2 kinetic model. The simulation was performed using a Runge-Kutta 4<sup>th</sup> order numerical integration method, programmed using the Mathcad engineering calculations software (Mathsoft, PTC). For the sake of comparison, the simulated curve has been analyzed using the same model-fitting method employed in Juhasz *et al.*<sup>[1]</sup> Figure 2 shows the plots resulting from fitting the data to some of the most used ideal models in the literature. The activation energies and preexponential factors calculated from the plots, as well as the regression coefficients for each case, have also been included in the figures. As it can be observed, the activation energy obtained is highly dependent on the kinetic model assumed, but only the fit to A2 yields the correct value. Out of the eight models tested, four deliver excellent fits to the simulated data while the other four are still reasonably good. Thus, from those results, it could be concluded that it is not possible to determine the correct model from a single linear heating curve. Note that this conclusion is reached after analyzing simulated, error-free data. When using experimental data it is possible that even a higher percentage of the tested models could adequately fit such data. Thus, in order to unambiguously determine the kinetic parameters by a model-fitting procedure, a set of experimental curves, each recorded under different heating schedules, should be employed.<sup>[8, 9]</sup>

The critical importance of determining the correct kinetic triplet cannot be overstated, especially when the prediction of the shelf-life of products or materials is the ultimate objective. As an example, we can consider a material decomposing according to the kinetic parameters used for simulating the curve in Figure 1. The shelf-life estimation can be performed using the following equation<sup>[8]</sup>:

$$t_{\alpha} = \frac{g(\alpha)}{Ae^{-E/RT}} \quad (1),$$

where  $t$  is the time for a certain conversion  $\alpha$  to be reached,  $A$  is the preexponential factor,  $E$  the activation energy,  $R$  the gas constant and  $g(\alpha)$  the integral form of the kinetic model. The algebraic functions corresponding to the different kinetic models can be found elsewhere.<sup>[3, 4]</sup> Table 1 shows the estimated time needed for 10% of the initial material ( $\alpha = 0.1$ ) to decompose at a temperature of 50°C, calculated using eq. (1) and the different kinetic triplets deduced from each of the fits in Figure 2. If the simulated data is fitted to an A2 kinetic model, that is the correct one, a shelf-life of 5.6 days is obtained. On the other hand, if data are fitted to any other model, shelf-lives ranging from  $10^4$  to  $10^{15}$  days are obtained. Thus, it is clear that the shelf-life would be grossly overestimated if the wrong model is selected.

In summary, while we consider EGA-Li<sup>+</sup>IAMS technique constitutes an interesting alternative to the most conventional thermogravimetry (TGA) for the kinetic analysis of thermal degradation processes, the kinetic analysis procedures must still be properly employed, according to the guidelines recently suggested by the ICTAC Kinetics Committee.<sup>[8]</sup> Thus, in the case of non-isothermal experiments, multiple runs recorded under different heating profiles are needed to unambiguously determine the kinetic parameters.

## ACKNOWLEDGEMENT

Financial support from project CTQ2011-27626 (Spanish Ministerio de Economía y Competitividad) and FEDER funds is acknowledged. Additionally, one of the authors (PESJ) is supported by a JAE-Doc grant (CSIC-FSE).

## References

- [1] M. Juhasz, S. Takahashi, Y. Kitahara, T. Fujii. Thermal decomposition of pyridoxine: an evolved gas analysis-ion attachment mass spectrometry study. *Rapid Communications in Mass Spectrometry*. **2012**, 26, 759.
- [2] A. Khawam, D. R. Flanagan. Solid-state kinetic models: Basics and mathematical fundamentals. *J. Phys. Chem. B*. **2006**, 110, 17315.
- [3] P. E. Sanchez-Jimenez, L. A. Perez-Maqueda, A. Perejon, J. M. Criado. A new model for the kinetic analysis of thermal degradation of polymers driven by random scission. *Polymer Degradation and Stability*. **2010**, 95, 733.
- [4] A. Perejon, P. E. Sanchez-Jimenez, J. M. Criado, L. A. PerezMaqueda. Kinetic Analysis of Complex Solid State Reactions. A New Deconvolution Procedure. *J. Phys. Chem. B*. **2011**, 115, 1780.
- [5] M. Maciejewski. Computational aspects of kinetic analysis. Part B: The ICTAC Kinetics Project - the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. *Thermochim. Acta*. **2000**, 355, 145.
- [6] M. E. Brown. Steps in a minefield - Some kinetic aspects of thermal analysis. *J. Therm. Anal.* **1997**, 49, 17.
- [7] J. M. Criado, A. Ortega. Remarks on the discrimination of the kinetics of solid-state reactions from a single non-isothermal trace. *J. Therm. Anal.* **1984**, 29, 1225.
- [8] S. Vyazovkin, A. K. Burnham, J. M. Criado, L. A. Perez-Maqueda, C. Popescu, N. Sbirrazzuoli. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta*. **2011**, 520, 1.
- [9] L. A. Perez-Maqueda, J. M. Criado, J. Malek. Combined kinetic analysis for crystallization kinetics of non-crystalline solids. *J. Non-Cryst. Solids*. **2003**, 320, 84.

## Figure Captions.

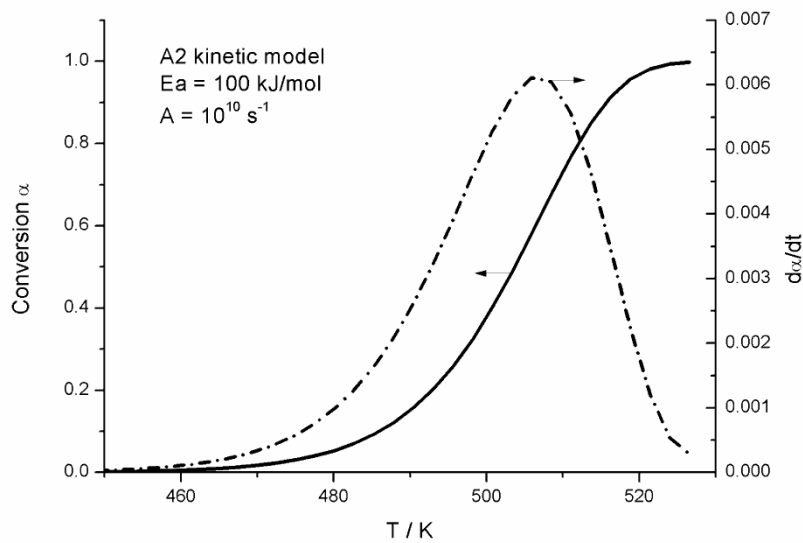
**Figure 1.** Kinetic curves simulated according the following kinetic parameters:  $E_a=100\text{kJ/mol}$ ,  $A=10^{10}\text{ s}^{-1}$ , and an A2 kinetic model.

**Figure 2.** Plots obtained from fitting the simulated curve in Figure 1 to some of the most usual kinetic models by means of a differential model-fitting procedure, as employed by Juhasz.<sup>[1]</sup> The activation energy is calculated from the slope of the curves and the preexponential factor from the intercept.

**TABLE 1.** Shelf-life prediction at 50°C, determined using eq. (1) and the kinetic parameters obtained from fitting the data extracted from a simulated curve ( $E_a=100\text{kJ/mol}$ ,  $A=10^{10}\text{ s}^{-1}$ , A2 kinetic model) to different kinetic models, as shown in Figure 2.

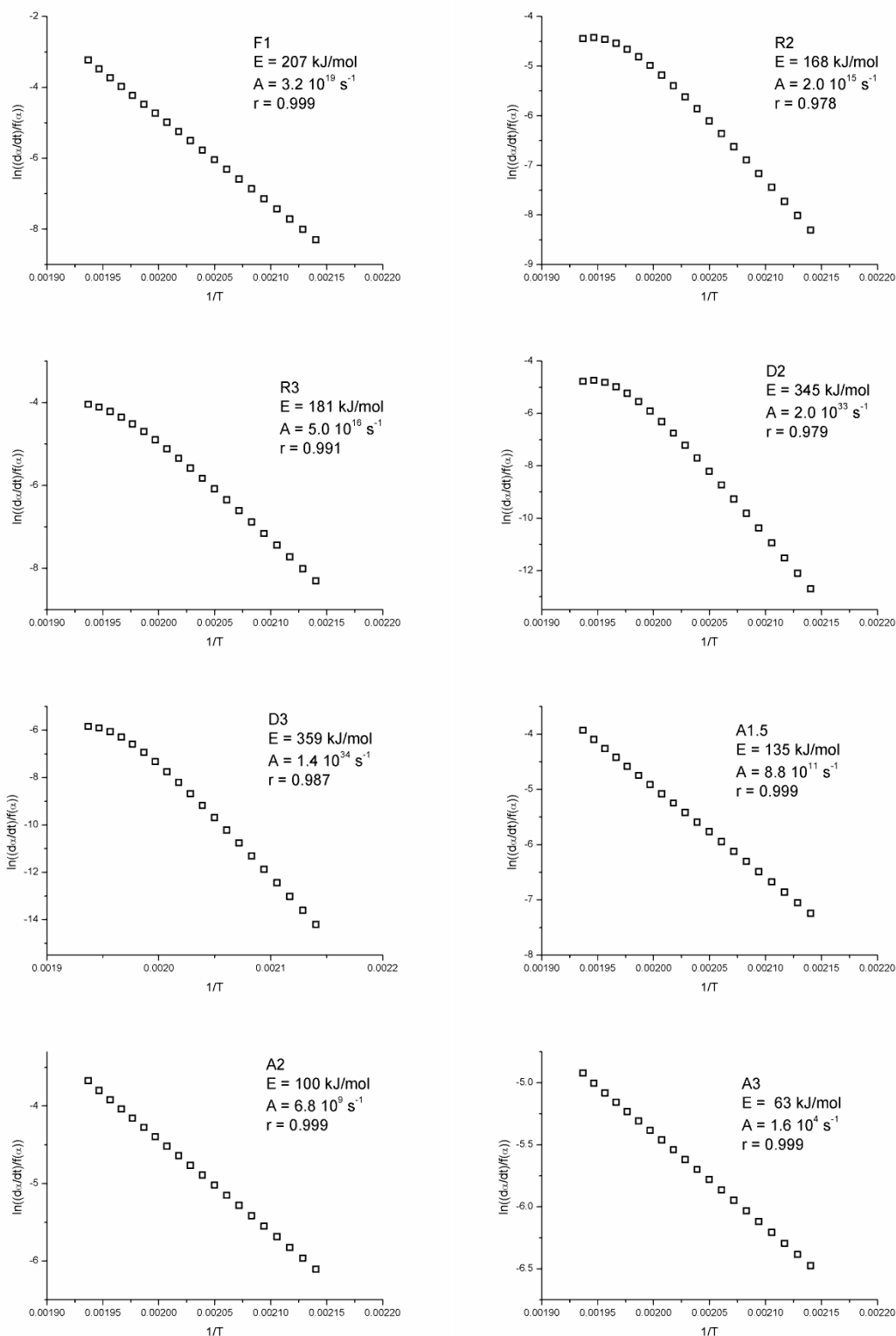
Model	F1	R2	R3	D2	D3	A1.5	A2	A3
$t_{90\%}(\text{days})$	$1.2 \cdot 10^8$	$9.0 \cdot 10^5$	$4.6 \cdot 10^6$	$1.9 \cdot 10^{15}$	$1.2 \cdot 10^{16}$	$2.0 \cdot 10^4$	5.6	5.1

**FIGURE 1**



**Figure 1.** Kinetic curve simulated according to the following kinetic parameters:  $E_a=100\text{kJ/mol}$ ,  $A=10^{10}\text{ s}^{-1}$ , and an A2 kinetic model.

**FIGURE 2**



**Figure 2.** Plots obtained by fitting the simulated curve in Figure 1 to some of the most usual kinetic models. The fits have been carried out using the same differential model-fitting procedure employed by Juhasz *et al.* [1] The activation energy is calculated from the slope of the curves and the preexponential factor from the intercept.

