

# **THERMOKINETICS OF THE ETHYL ACETATE ACID AND ALKALINE HYDROLYSIS BY DIFFERENTIAL SCANNING CALORIMETRY**

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## **Abstract**

The kinetic investigation of thermoanalytical curves for the ethyl acetate and alkaline hydrolysis, requires tedious calculations of several mathematical expressions, to establish the correlation between the thermochemical and kinetic parameters. Using the DSC measured data for the heat flow-temperature dependence of the studied reactions, we have obtained the kinetic bulk parameters and the dependence  $k = k(T)$  for the basic and acid hydrolysis of ethyl acetate.

**Keywords:** DSC, ethylacetate hydrolysis, thermokinetics

## **Introduction**

Recent studies have opened new perspectives to the development of thermokinetics, by extending the DSC to the chemical reactions kinetic characterization. The research devoted to the initiation of the correlations between the thermal parameters characteristic to the physico-chemical processes and their kinetic peculiarities, were performed by Borchhardt and Daniels [1] and more recently, by Urichek [2] and Hoffmann, as well as Kretzschmar and Koster [3]. However, it should be specified that the majority of the scientific papers published before our research works and approaches in the same method, were oriented to epoxy resin processes [4–8].

### *DSC data correlation with the kinetic reaction parameters*

In principle, the correlation between the reaction thermodynamic parameters and its kinetic parameters express the proportionality of the heat flow,  $dH/dt$ , with the total reaction enthalpy,  $\Delta H$  and the conversion degree,  $\alpha$  at a given time.

Thus, for a reaction of the  $n$  order, we get:

$$\frac{dH_i}{dt} = k\Delta H(1 - \alpha)^n \quad (1)$$

where  $\alpha = \frac{\Delta H_i}{\Delta H}$ ; the reaction enthalpy at a given moment,  $\Delta H_i = \sum_{i=0}^j \frac{dH_i}{dt}$ , and

the total enthalpy,  $\Delta H = \sum_{i=0}^{\infty} \frac{dH_i}{dt}$ .

From Eq. (1) and from the quantities already formulated, follows the reaction non-isothermal rate constant, obtained in the dynamic temperature regime, assured by the experimental method employed:

$$k = \frac{1}{\Delta H} \cdot \frac{dH_i}{dt} \left/ \left( 1 - \frac{\Delta H_i}{\Delta H} \right)^n \right. \quad (2)$$

The quantities in Eq. (2) are deduced from the DSC curves, recorded in the  $dH/dt = f(T)$  coordinates, for the characterised processes. In a logarithmic form, Eq. (2) may be equaled to the classical Arrhenius relation:

$$\ln k = \ln A - \frac{E}{RT} \quad (3)$$

thus introducing in the resulting relation, two more kinetic parameters: the reaction activation energy,  $E$ , and the frequency factor,  $A$ :

$$\ln \left( \frac{1}{\Delta H} \cdot \frac{dH_i}{dt} \right) = \ln A + n \ln \left( 1 - \frac{\Delta H_i}{\Delta H} \right) - \frac{E}{RT_i} \quad (4)$$

By applying the multilinear regression method to the latter equation, a linear equations system is got, symbolized by:

$$y_i = x_{i1} \ln A + x_{i2}n + x_{i3}E \quad (5)$$

$i = 1, 2, 3, \dots, j$ .

Therefore:  $x_{i1} = 1$ ;  $x_{i2} = \ln \left( 1 - \frac{\Delta H_i}{\Delta H} \right)$ ; and  $x_{i3} = -\frac{1}{RT_i}$

$$y_i = \left( \frac{1}{\Delta H} \cdot \frac{dH_i}{dt} \right) \quad (5a)$$

The system is transposed in a matricial form:

$$\begin{array}{c} \left( \begin{array}{c} y_1 \\ y_2 \\ \cdot \\ \cdot \\ \cdot \\ y_j \end{array} \right) = \begin{array}{c} \left| \begin{array}{ccc} x_{11} & x_{12} & x_{13} \\ x_{21} & x_{22} & x_{23} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ x_{j1} & x_{j2} & x_{j3} \end{array} \right| \left( \begin{array}{c} \ln A \\ n \\ E \end{array} \right) \\ R \\ X_j \end{array}$$

The bulk kinetic parameters  $X_j(\ln A, E$  and  $n)$  are calculated, based on Cramer's rule, with the relation:

$$X_j = \frac{1}{d} \sum_{i=1}^3 R_{ij} C_i ; \quad j = 1, 2, 3.$$

( $d$  is the determinant in the  $R$  matrice).

The rate constant  $k$  (see Eq. 2) can be restrictedly formulated, in close correlation with the  $A$  area below the DSC curve, in the temperature range corresponding to a complete evolution of the reaction ( $A = \Delta H$ ) and with the partial area ( $a = \Delta H_i$ ), delimited by the curve and the parallel to the ordinate in the relevant point on the temperature axis. Thus:

$$k = \frac{\frac{dH_i}{dt} A^{n-1}}{(A-a)^n} \quad (6)$$

In this case the activation energy and the reaction frequency factor can be calculated based on a procedure presented by Hoffmann and co-workers [3]. The DSC data obtained were used also in the application, of a variant to Freeman and Carrol's classical theory in this form:

$$\frac{\ln \left( \frac{dH_{i+1}}{dt} \cdot \frac{dt}{dH_i} \right)}{\ln \left( \frac{\Delta H - \Delta H_{i+1}}{\Delta H - \Delta H_i} \right)} = n - \frac{E}{R} \frac{T_i - T_{i+1}}{T_i T_{i+1} \ln \left( \frac{\Delta H - \Delta H_{i+1}}{\Delta H - \Delta H_i} \right)} \quad (7)$$

$$x_i = \frac{1}{R} \frac{T_i - T_{i+1}}{T_i \cdot T_{i+1} \ln \frac{\Delta H - \Delta H_{i+1}}{\Delta H - \Delta H_i}} \quad (7a)$$

and

$$y_i = \frac{\ln \left( \frac{dH_{i+1}}{dt} \cdot \frac{dt}{dH_i} \right)}{\ln \left( \frac{\Delta H - \Delta H_{i+1}}{\Delta H - \Delta H_i} \right)} \quad (7b)$$

In the graphical representation  $y = f(x)$ , you get the straight line  $y = n - Ex$ . The activation energy results from its inclination, while the ordinate, at its origin is equal to the reaction order. The preexponential factor is calculated from the relation:

$$\ln A = \ln \left( \frac{d\tilde{H}}{dt} \cdot \frac{1}{\Delta H} \right) - n \ln \left( 1 - \frac{\Delta\tilde{H}}{\Delta H} \right) + \frac{E}{RT} \quad (8)$$

The tilde-marked quantities are averages on the temperature range considered.

## Results and comments

An example of correlating the data got by differential scanning calorimetry with the kinetic parameters, is offered by ethyl acetate hydrolysis studied both in acid and alkaline medium. It should be specified that the thermokinetics of these reactions was checked by traditional, anisothermal calorimetry, too, much more tedious than the DSC, but with satisfactory results.

The calorimeter used in this work was a Perkin-Elmer (DSC) one. The samples used for these experiments were of the  $10^{-5}$  mg order of magnitude for the ethyl acetate, the calorimeter efficiency being of  $2 \text{ kcal}\cdot\text{sec}^{-1}$  for a dynamic temperature regime of  $10 \text{ deg}\cdot\text{min}^{-1}$ . The recommended temperature correction,  $T_{\text{real}} = T_{\text{obs}} - 0.085 \text{ d}T/\text{d}t + 0.85$ , being zero. The recording paper unwinding rate was set at  $10 \text{ mm}\cdot\text{min}^{-1}$ . The procedure took place in argon atmosphere, after a previous calibration with metallic indium. The DSC curves recorded are shown in Fig. 1, for the reaction taking place in alkaline medium (a) and in acid medium (b).

The results obtained, processed according to the Eqs (5) and (7a,b) are presented in Table 1.

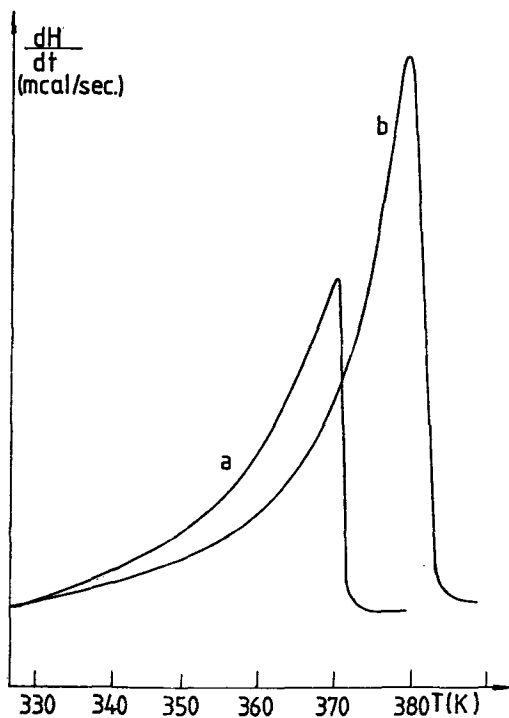


Fig. 1 Ethyl acetate hydrolysis. DSC curves in alkaline (a) and acid (b) medium

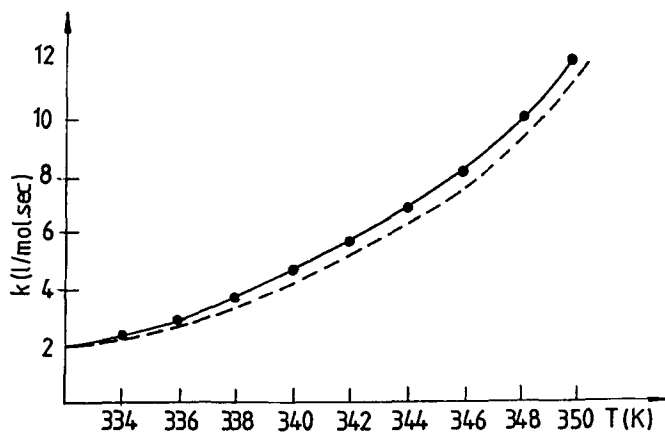


Fig. 2 Rate constant variation with the temperature for the applied methods – in the alkaline hydrolysis

**Table 1** Kinetic parameters of the ethyl acetate hydrolysis

Kinetic parameters	Alkaline hydrolysis		Acid hydrolysis	
	Eq. (5)	Eq. (7a, b)	Eq. (5)	Eq. (7a, b)
$\ln A$	23	23.70	11	11.15
$E$ (kcal/mol)	23.42±1.20	23.60± 0.90	12.92±1.35	13.06±0.94
$n$	2.07± 0.11	1.99± 0.22	1.00± 0.13	1.00±0.11

**Table 2** Rate constant variation with the temperature

$T / K$	Alkaline hydrolysis		Acid hydrolysis	
	Method (1)	Method (2)	Method (1)	Method (2)
	$k / \text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$		$k / \text{s}^{-1}\cdot 10^4$	
334	2.3	2.42	—	—
336	2.84	3.00	2.25	2.22
338	3.49	3.71	2.50	2.49
340	4.29	4.57	2.79	2.79
342	5.26	5.62	3.12	3.13
344	6.43	6.88	3.47	3.50
346	7.83	8.43	3.86	3.91
348	9.53	10.28	4.29	4.36
350	11.56	12.53	4.77	4.86
352	—	—	5.29	5.41
354	—	—	5.85	6.01

(1) The method of multilinear regression

Studying the variation of the rate constants with the temperature, as they are shown in Table 2, we can see, on the one hand, concordant values between the constants calculated, based on the presented methods, for both reactions, and on the other hand, an exponential dependence  $k = k(T)$  more obviously evidenced graphically.

As an example was presented the  $k = k(T)$  dependence, for the second order process ( the alkaline hydrolysis), in the Fig. 2.

The concordance between the  $k$  values is satisfactory, in this case, but for the acid hydrolysis, reaction of the first order, the concordance of the  $k$  values got at various temperatures, is higher. In both cases the agreement between the rate constants, calculated by the presented methods are better at lower temperatures, the deviations being observed with the increase of the temperature.

## Conclusions

The experimental facilities and the accuracy of the DSC data are fundamental elements, ready to provide incentives to the non-isothermal kinetics research, even if it was to be limited to the reactions having a simple mechanism. We do not exclude the possibility to extend the thermokinetic research to more complicated reaction mechanisms, but this involves experimental complications and theoretical adjustments.

The actual stage of the thermokinetic research allows only the bulk kinetic parameters of a chemical process to be ascertained.

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**Zusammenfassung** — Kinetische Untersuchungen der thermoanalytischen Kurven der sauren und basischen Hydrolyse von Ethylacetat erfordern monotone Berechnungen einiger mathematischer Ausdrücke, um eine Korrelation zwischen thermochemischen und kinetischen Parametern herzustellen. Unter Verwendung der gemessenen DSC-Daten für die Wärmefluß-Temperaturabhängigkeit der untersuchten Reaktionen erhielten wir die kinetischen Gesamtparameter und die Abhängigkeitsfunktion  $k=k(T)$  für die basische und saure Hydrolyse von Ethylacetat erhalten.