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NON-ISOTHERMAL KINETIC STUDY OF THE HETEROGENEOUS THERMAL DECOMPOSITION OF A MANNICH COMPOUND

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Abstract

The authors present data concerning the evaluation of kinetic parameters of the decomposition of a Mannich compound by using the classical method of constant heating rate thermal analysis and the new one of controlled rate thermal analysis (CRTA). The data processed using the CRTA method allow to obtain more reliable kinetic parameters according to the proposed reaction mechanism.

Keywords: kinetics, Mannich compounds, thermal decomposition

Introduction

The kinetic analysis of the heterogeneous decomposition of solids or melted organic compounds in solid-gas systems can be fulfilled by:

– observing the isothermal evolution in time of the gases evolved in reaction at constant pressure or volume,

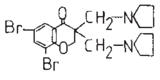
– observing the mass of the compound that decomposes as a function of temperature which change in time according to a linear program of heating,

– observing the mass of the compound that decomposes as a function of temperature which changes so that the decomposition rate is kept at a constant value; this last procedure, called controlled rate thermal analysis (CRTA) and used first by Erdey, Paulik, Paulik [1] and Rouquerol [2] began to be largely applied only after 1983 [3].

In this report, we present the results of a heterogeneous decomposition kinetics of a Mannich compound in classical conditions (constant heating rate) as well as in CRTA conditions.

Experimental

The study was performed using the powder of the Mannich Compound



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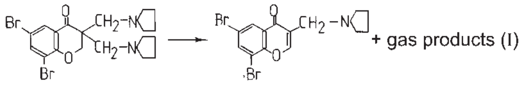
synthesized and analyzed by Finaru *et al.* [4]. The thermal analysis curves at constant heating rate were obtained by help of a derivatograph Paulik-Paulik-Erdey type Q-1500D and a Paulik-Paulik-Erdey derivatograph type C equipped with computer. The samples were heated in air in the temperature range 20–220ºC with a heating rate of 1.82 K min^{-1}. The curves temperature-conversion in CRTA conditions were obtained with the derivatograph type C.

In order to obtain the values of the kinetic parameters, the experimental data obtained at constant heating rate and in CRTA conditions were processed by means of the various versions of the program VERSATILE [5]. The obtained kinetic parameters were used to simulate thermogravimetric curves in (α, *T*) coordinates, and isokinetic curves (*T*, α). The computer program allows the fitting of the experimental points on the simulated curves.

Results and discussion

The decomposition of the Mannich compound with constant heating rate

The heating of the Mannich compound with a rate of 4.82 K min^{-1} leads to its melting at 136ºC and a first step of decomposition in the range 180–220ºC due to the reaction:



The TG and DTG curves associated to this step of decomposition correspond to a single process and they can be kinetically processed. The further heating of the product from reaction I leads to an oxidative degradation, process that cannot be kinetically processed.

Three integral methods were applied for the kinetic analysis of the constant heating rate experimental data: Coats-Redfern [6], Flynn-Wall [7] and Urbanovici-Segal [8], the last one being a modified variant of the Coats-Redfern method. All the three integral methods are based on a form of the conversion function corresponding to the 'reaction order' model. The obtained values for the kinetic parameters of reaction I are listed in Table 1.

Table 1 Values of the kinetic parameters of reaction I (β=4.82 K min^{-1})

Method	Order of reaction/ *n*	Activation energy/ kJ mol^{-1}	Preexponential factor/ s^{-1}	Correlation coefficient/ *r*
Coats-Redfern	1.50	406	$6.12\cdot10^{42}$	0.9958
Flynn-Wall	1.50	393	$9.05\cdot10^{41}$	0.9960
Urbanovici-Segal	1.40	393	$2.15\cdot10^{41}$	0.9957

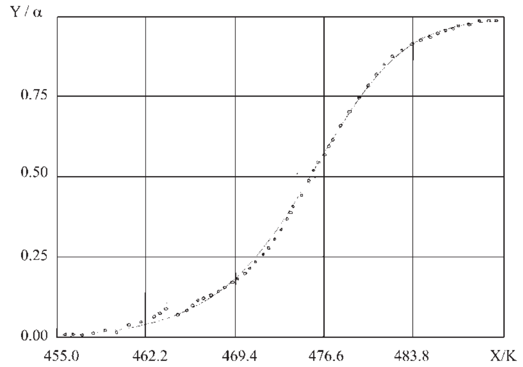


Fig. 1 Experimental curve ∘∘∘∘ and calculated curve – for reaction I

By using the values of the kinetic parameters obtained by the Coats-Redfern method the curve (α, T) was simulated. The experimental points were put on the simulated curve (Fig. 1). They fit quite well the curve.

The thermal decomposition of a Mannich compound with constant reaction rate

The results obtained in constant heating rate conditions (mainly the high values of the activation parameters) suggested to use the CRTA method in order to describe the decomposition kinetics better. This method allows to obtain results free of thermal and mass transfer limitations. Using this technique we can evaluate the kinetic parameters for a more general conversion function, such as for the autocatalytic reactions expressed by:

$$f(\alpha)=\alpha^{m}(1-\alpha)^{n} \tag{1}$$

where α is the conversion degree and the exponents m and n are characteristic constant of the conversion function. For m=0 the Eq. (1) becomes the rate equation corresponding to the 'reaction order' model.

The kinetic parameters of the thermal decomposition were evaluated by using an original method [5]. This method uses two CRTA curves obtained for two different constant reaction rates. For the decomposition rates $d\alpha/dt$ of $8.68\cdot10^{-5}$ s^{-1} and $1.70\cdot10^{-4}$ s^{-1} the following kinetic parameters were obtained:

$E = 90.7$ kJ mol^{-1}
$A = 5.24\cdot10^{7}$ s^{-1}
$n = 1.17$
$m = 0.44$

The simulated curves (T, α) for the two reaction rates and the experimental data are presented in Fig. 2. The experimental data fit satisfactorily the simulated curves thus confirming the correctness of the kinetic parameters obtained by CRTA method.

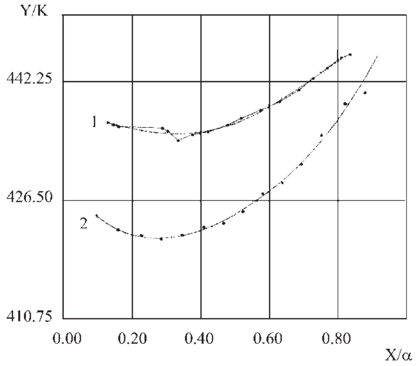


Fig. 2 Experimental curves ···· and calculated curves – for the decomposition rates $1.70\cdot10^{-4}$ s^{-1} (1) and $8.68\cdot10^{-5}$ s^{-1} (2)

This conclusions can be drawn considering the values of the activation parameters that correspond to normal values for this type of heterogeneous reaction.

The good correlation between the experimental data and the form of Eq. (1) suggests that the thermal decomposition of the investigated Mannich compound is an autocatalytic reaction.

Conclusions

1. The kinetics of the non-isothermal decomposition of a Mannich compound was studied under the conditions of constant heating rate as well as constant reaction rate.

2. The results obtained with constant heating rate may be altered by mass and heat transfer processes.

3. Using the CRTA method, reliable results were obtained for the kinetic parameters which suggests an autocatalytic reaction.

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