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DETERMINATION OF ACTIVATION ENERGIES BY USING DIFFERENT FACTORS Φ IN ADIABATIC CALORIMETRY*

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Abstract

Traditionally, the kinetic treatment of adiabatic calorimetry data has been based on the results of one or more experiments, but always with the assumption of the kinetic model that the reaction follows to calculate the kinetic parameters. In this paper a method for the determination of the activation energy that uses a set of adiabatic calorimetry data is developed. To check the method, the thermal decompositions of two peroxides were studied.

Keywords: adiabatic calorimetry, kinetics, Kissinger method

Introduction

The information obtained by adiabatic calorimetry may be classified into two groups:

– Thermodynamic information, such as $\Delta_{ad}T$, $\Delta_r H$, p_{max}, T_{max} and the maximum rate of temperature rise. In general, this is information relating to the reaction severity.

– Kinetic information, activation energy, frequency factor and kinetic model.

Each kind of information implies a different experimental design. When an experiment is performed to obtain thermodynamic information, the objective of the experiment is usually to evaluate the maximum violence of the process or the vent sizing. Under these conditions, the factor Φ, defined in Eq. (1), should be as close as possible to one:

$$\Phi = \frac{m_s c_{ps} + m_c c_{pc}}{m_s c_{ps}} \tag{1}$$

When the required information is the kinetics of the process, the objective of the experiments is to obtain the kinetic model and its parameters that allow reproduction of the experimental data, and simulation of the behaviour of the system under differ-

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ent conditions. These studies involve two problems: there is a considerable influence of noise at a low self-heating rates, so low Φ values (close to 1) seem to be the best choice to monitor the beginning of the reaction; on the other hand, high self-heating rates produce distortion of the curves, and higher Φ values (more than 2) might be used to follow the complete exotherm. The suggestion is to use factors Φ as low as possible, but not too low.

Traditionally, the kinetic treatment of adiabatic calorimetry data assumes a kinetic model to calculate the kinetic parameters. The kinetic parameters obtained in this way may be meaningless, and they may produce an incorrect simulation of the behaviour of the system under different conditions.

The aim of this paper is to develop a procedure with which the activation energy of the process can be obtained without assumption of the kinetic model. This procedure will furnish more realistic values of the activation energy.

Theory

Some thermal analysis (TA) techniques such as differential scanning calorimetry (DSC), use more than one curve to obtain the kinetic parameters. In this kind of method, the activation energy is calculated in a previous stage, and once it is known, the kinetic model can be found, so no previous definition of the kinetic model is required.

One of the most popular methods in TA was that developed by Kissinger [1]. The method is based on the fact that the temperature of the maximum of a DSC curve increases with the heating rate. This variation can be explained theoretically and is a function of the activation energy.

The general expression for the reaction rate of a simple process is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{e}^{-\mathrm{E/RT}}g(\alpha) \tag{2}$$

where $g(\alpha)$ symbolizes the kinetic model, and α, the degree of conversion, is defined as

$$\alpha = \frac{\int_{\mathrm{o}}^{\mathrm{t}} \dot{Q}\mathrm{d}t}{\int_{\mathrm{o}}^{\infty} \dot{Q}\mathrm{d}t} \tag{3}$$

In dynamic DSC, temperature and time are related by the heating rate: $\beta = \mathrm{d}T/\mathrm{d}t$. The Kissinger method is based on study of the temperature at which the maximum reaction rate appears. At this point $\mathrm{d}^2\alpha/\mathrm{d}t^2$ vanishes, leading to

$$\frac{E\beta}{RT_{\mathrm{p}}^2} g(\alpha_{\mathrm{p}}) = -g'(\alpha_{\mathrm{p}})\frac{\mathrm{d}\alpha}{\mathrm{d}t};\ \ g'(\alpha_{\mathrm{p}}) = \left(\frac{\mathrm{d}g(\alpha)}{\mathrm{d}\alpha}\right)_{\mathrm{p}} \tag{4}$$

and

$$\frac{\beta}{T_p^2} = -\frac{AR}{E} g'(\alpha_p) e^{-E/RT_p} \tag{5}$$

and, finally, to the well-known Kissinger equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(-\frac{AR}{E} g'(\alpha_p)\right) - \frac{E}{RT_p} \tag{6}$$

where the expression $AR/Eg'(\alpha_p)$ is assumed to be a constant.

The same idea can be applied to adiabatic calorimetry data. In DSC the temperature at the point of maximum heat release increases with the heating rate, whereas in adiabatic calorimetry this temperature increases as the factor Φ decreases. Thus, if adiabatic calorimetry experiments are performed with different factors Φ, it might be possible to obtain the activation energy.

In adiabatic calorimetry, the general expression for the reaction rate is the same as Eq. (2), but, with the assumption that the heat capacity of the system remains constant throughout the reaction, a more convenient definition of the degree of conversion is employed:

$$\alpha = \frac{T - T_o}{\Delta T} \quad \text{or} \quad \frac{d\alpha}{dt} = \frac{1}{\Delta T}\frac{dT}{dt} \tag{7}$$

Thus, the rate of temperature rise is not a constant, as it is in dynamic DSC, and at the maximum it has to be expressed as $(dT/dt)_p$.

Study of the maximum point produces the expression

$$\frac{d^2\alpha}{dt^2} = \frac{E}{RT_p^2} A e^{-E/RT_p} \left(\frac{dT}{dt}\right)_p g(\alpha_p) + A e^{-E/RT_p} g'(\alpha_p) \left(\frac{d\alpha}{dt}\right)_p = 0 \tag{8}$$

On introduction of the expression for the reaction rate, Eq. (2):

$$\frac{E}{RT_p^2}\left(\frac{dT}{dt}\right)_p = -g'(\alpha_p) A e^{-E/RT_p} \tag{9}$$

Finally, the expression that leads to the activation energy from a set of adiabatic experiments is inferred:

$$\ln\left(\frac{1}{T_p^2}\left(\frac{dT}{dt}\right)_p\right) = \ln\left(-\frac{AR}{E} g'(\alpha_p)\right) - \frac{E}{RT_p} \tag{10}$$

It should be pointed out that the expression obtained for adiabatic conditions is similar to the Kissinger equation, but the heating rate β is replaced by the self-heating rate dT/dt, both at the temperature of maximum heat release.

Equation (10) therefore allows the calculation of the activation energy from a set of adiabatic experiments performed with different factors Φ through a simple linear regression of $\ln(1/T_p^2(dT/dt)_p)$ *vs.* $1/RT_p$. Now it is possible to apply a methodology that allows the development of a kinetic model that better fits the experimental data [2].

The first step in this method is to multiply the experimental values of the reaction rate by $e^{E/RT}$; this yields the function $Y(\alpha)$, which is proportional to the kinetic model $g(\alpha)$ and has the same shape:

$$Y(\alpha) = \frac{d\alpha}{dt} e^{E/RT} = Ag(\alpha) \tag{11}$$

The shape of $Y(\alpha)$ contains information about the kinetic model. For example, in the most simple case, if the function $Y(\alpha)$, normalized within (0,1), *vs.* α is a straight line with slope equal to –1, then the kinetic model should represent a first-order reaction.

Experimental

To check the validity of the method, the thermal decompositions of two peroxides were studied. The selected substances were 2,5-dimethyl-2,5-di(tert)butylperoxy)hexane (DHBP) and di-tert-butyl peroxide (DTBP). Both decompositions were studied by using the adiabatic calorimeter PHI-TEC II from H.E.L.

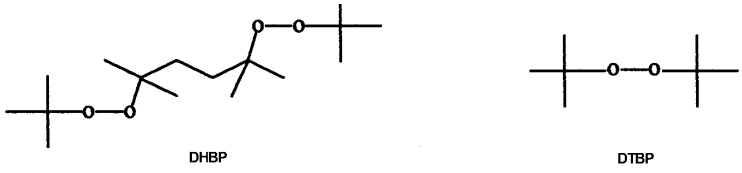

Fig. 1 Chemical structures of DHBP and DTBP

Study of DHBP

Nine adiabatic experiments were carried out with thin-walled stainless steel (SS) and glass cans. The results are presented in Table 1.

Figure 2 shows the evolution of temperature as a function of time for the experiments. The application of the developed method, Eq. (10), leads to a straight line as shown in Fig. 3. The slope of this line corresponds to an activation energy of 146±16 kJ mol^{-1}, while the activation energy obtained by the study of four DSC curves at different heating rates is 140±3 kJ mol^{-1}, the relative difference being about 4%. These DSC experiments are presented in Fig. 4. In this case, a dispersion of the points is observed, which could be due to the very high heating rates obtained or to the fact that the experiments were carried out with different types of cells.

Table 1 Experimental conditions and results of DHBP test

Experiment	Can type	Φ	T_o/	T_f/	T_p/	$(dT/dt)_p$/
			°C			K min^{-1}
1	SS	4.18	114.5	233.7	222.2	1026
2	SS	5.85	112.3	188.4	179.9	24
3	SS	5.09	111.2	208.5	195.1	125
4	SS	5.36	115.0	208.5	184.7	26
5	SS	4.70	113.0	216.4	208.7	90
6	glass	4.76	112.4	233.5	202.3	375
7	glass	4.75	114.5	234.1	209.6	382
8	glass	5.55	116.3	210.1	196.0	68
9	glass	5.10	114.0	240.0	201.1	334

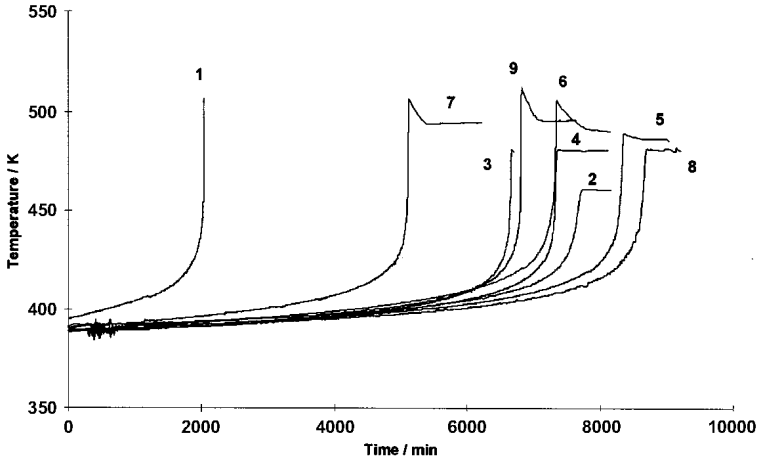

Fig. 2 Temperature as a function of time for the thermal decomposition of DHBP under adiabatic conditions

Study of DTBP

The experiments were carried out with thin-walled SS cans of 100 mL. The characteristic parameters of the experiments and the results are listed in Table 2.

The evolution of temperature as a function of time is presented in Fig. 5. The application of the developed method, Eq. (10), leads to an activation energy of 167±6 kJ mol^{-1} (Fig. 6). This result is in good agreement with the literature [3] value of 158±5 kJ mol^{-1}. The relative difference is about 5%.

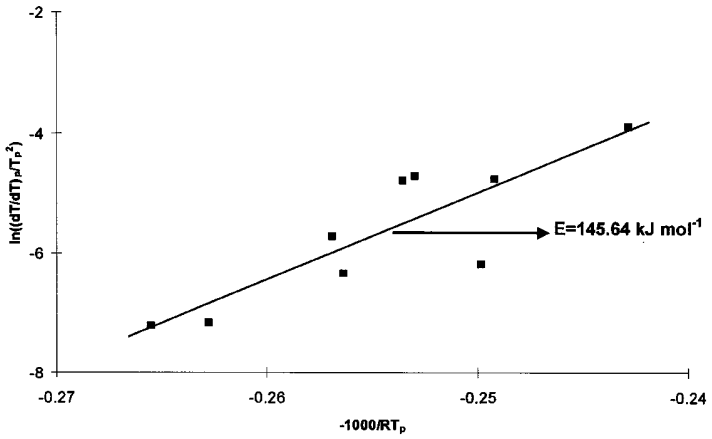

Fig. 3 Development of the activation energy in the thermal decomposition of DHBP

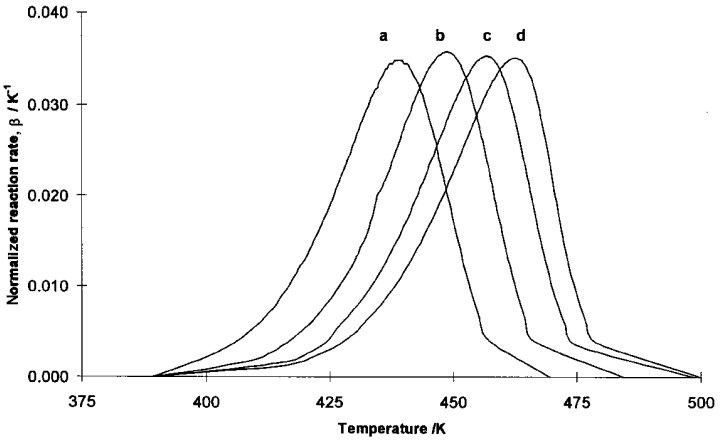

Fig. 4 Dynamic DSC experiments on the thermal decomposition of DHBP. The reaction rate is normalized by division by the corresponding heating rate: a – 2 K min^{-1}, b – 5 K min^{-1}, c – 10 K min^{-1} and d – 15 K min^{-1}

Table 2 Experimental conditions and results of DTBP test

Experiment	Φ	T_o/	T_f/	T_p/	$(dT/dt)_p$/ K min^{-1}
		°C			
1	1.09	130.0	253.1	214.0	759
2	1.18	116.9	243.2	228.0	385
3	1.10	115.3	226.1	237.8	103

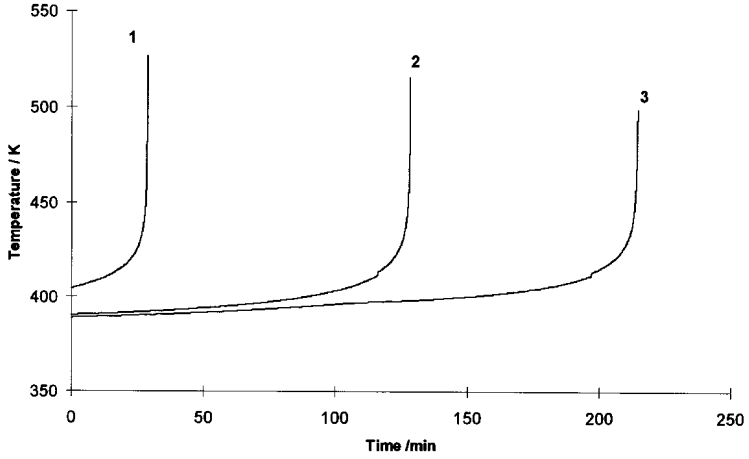

Fig. 5 Temperature as a function of time for the thermal decomposition of DTBP under adiabatic conditions

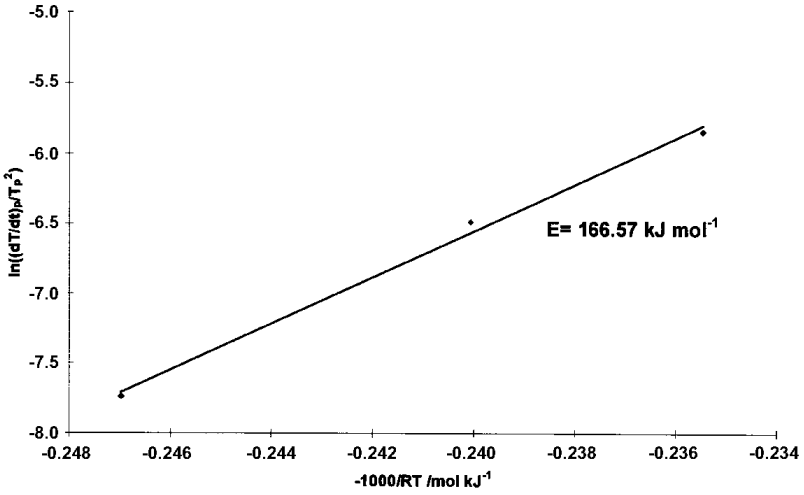

Fig. 6 Development of the activation energy in the thermal decomposition of DTBP

The kinetic model

The function $Y(\alpha)$ *vs.* the degree of conversion α is presented in Figs 7 and 8. Although there is a large influence of noise at low self-heating rates, which prevents normalization of the function, linear regression of the data gives a reasonably straight line, which implies that the kinetic model is a first-order reaction as found in the literature [3, 4].

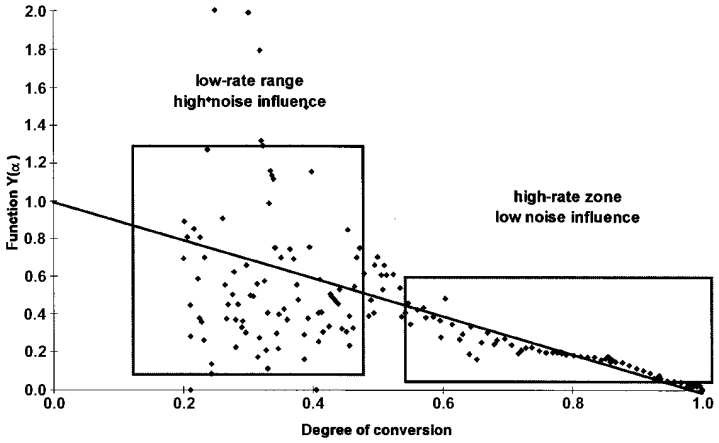

Fig. 7 Function $Y(\alpha)$ as a function of the degree of conversion α from experiment 8 on DHBP under adiabatic conditions

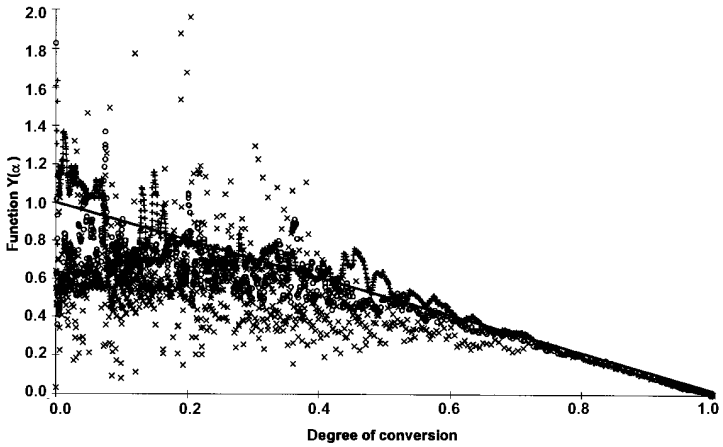

Fig. 8 Function $Y(\alpha)$ as a function of the degree of conversion α from three experiments on DTBP under adiabatic conditions

Conclusions

A method for evaluation of the activation energy by using a set of adiabatic calorimetry curves has been developed. The thermal decompositions of two peroxides have been studied with this method, the results being in good agreement with the literature and with the results obtained from DSC. The use of a set of adiabatic calorimetry curves results in more realistic kinetic studies, because it is not necessary a *priori* to assume the kinetic model to obtain the activation energy.

The main problem of the method is noisy data at low self-heating rates. Accordingly, improvements in the equipment to minimize noise would facilitate the kinetic analysis.

Nomenclature

A	Arrhenius frequency factor	s^{-1}
E	activation energy	$J\ mol^{-1}$
c_{pc}	specific heat of the adiabatic cell	$J\ kg^{-1}\ K^{-1}$
c_{pm}	specific heat of the sample	$J\ kg^{-1}\ K^{-1}$
Q	power released by the reaction	W
t	time	s
T	temperature	K

Greek symbols

α	degree of conversion	
β	reaction rate	$K\ s^{-1}$
Φ	adiabaticity factor	

Subscripts

f	final
o	initial
p	peak

* * *

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