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CALCULATION OF THE KINETIC PARAMETERS
Thermal decomposition of some phenol stabilizers on the basis of thermoanalytical data

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Abstract

The paper reports the calculation of kinetic parameters (activation energy, pre-exponent and reaction order) of thermodegradation of some phenol stabilizers. For this purpose, a software package for IBM-compatible personal computers is proposed. The first calculation of kinetic parameters (E, Z, n) was carried out for these compounds. The package can be applied for kinetic calculations on the thermodegradation of other substances.

Keywords: activation energy, degradation, phenol stabilizers, pre-exponent, reaction order

Introduction

Thermoanalytical methods of analysis are actively employed in research into the kinetics and mechanism of thermodegradation of various substances [1]. We have used non-isothermal methods to study the kinetics of degradation of spatially hindered phenols. Many compounds of this class are phenol stabilizers and find practical application as additives to light polymers to prevent the thermal-oxidative degradation of polymer matrices during processing and operation [2]. Stabilizers for specific application are empirically selected in most cases at present, though this problem can be attacked by employing chemical kinetics [3]. In this connection, a knowledge of the thermal properties and kinetic characteristics of analysis seems to be imperative, providing a justified approach to the selection of a specific stabilizer, especially as no data on degradation kinetic characteristics of the phenol stabilizers under investigation are available. Phenol stabilizers synthesized and characterized by the methods described in [4–6] are investigated in the present study. The spectral characteristics and the elemental analysis data correlate with the reported structural formulae (Table 1).

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Experimental

The kinetic parameters of thermodegradation of a set of phenol stabilizers were found in the present study; for this purpose, a mathematical program for the processing of experimental data was elaborated. Thermogravimetric curves obtained on a MOM derivatograph (Hungary) were used for the calculations [7]. To provide comparable and reproducible results, all samples were treated under strictly specified conditions valid for kinetic investigations: mass of sample 50 mg, temperature of maximum heating 500°C, and heating rate 5 K $\min^{-1}$, Al_2O_3 was used as the reference. The crucibles were platinum cups. Decomposition was conducted under an inert nitrogen atmosphere. The differential thermal curve (DTA) revealed clearly-defined endoeffects, appropriate to a) substance melting, occurring without mass change; and b) substance decomposition, concurrent with its mass change. Study of fusion at temperatures of 300–400°C and of the solid residue after thermodegradation up to 500°C indicated a mixture of decomposition products of the initial compound. We did not take substance volatility into consideration in the present study in view of papers [8, 9], where the volatility of phenol stabilizers with molecular mass more than 300 was shown to comprise less than 1% at 200°C [8].

Since the decomposition process takes place on fusion, it is possible to use an equation describing the kinetics of homogeneous processes to decide on a particular equation for kinetic parameter calculation:

$$\frac{d\alpha}{dt} = Z\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{1}$$

where t=time, α=degree of substance conversion, Z=constant (exponential factor of Arrhenius equation), E=activation energy, n=reaction order, R=gas constant, and T=temperature in K.

In our case, the heating was uniform and linear:

$$T = T_o + \beta t \tag{2}$$

where T_o=initial temperature and β=rate of temperature change. At the initial point of time $T=T_o$ and $\alpha=0$.

The elimination of time t from (1) with the aid of (2) results on integration in the following equations, covering the temperature dependence of the rate of substance decomposition:

$$\begin{aligned} \alpha(T) &= 1-\left[1-\frac{(1-n)Z}{\beta}J(T)\right]^{1/(1-n)}, \quad n \neq 1 \\ \alpha(T) &= 1-\exp\left[-\frac{Z}{\beta}J(T)\right], \quad n = 1 \end{aligned} \tag{3}$$

where

$$J(T) = \int_{T_o}^{T} e^{-R/Ru}\, du \tag{4}$$

The integral $J(T)$ represents a basis for mathematical model (1) and is calculated either numerically, or by using an approximation [10–16]. If factor T_o^2/T^2 is introduced on the right-hand side of Eq. (1), a new mathematical model of the process arises, which is not too different from the initial one for a reasonable distinction between T and T_o (especially at specific intervals between experimental points). The advantage of this mathematical model is its simplicity, as the integral $J(T)$ is taken in elementary functions and the following formula is valid:

$$J(T) = T_o^2 \int_{T_o}^{T} e^{-E/Ru} \frac{du}{u^2} = R\frac{T_o^2}{E}\left(e^{-E/RT} - e^{-E/RT_o}\right) \tag{5}$$

Both approaches are successful when the problem of determination of the kinetic parameters of the mathematical model under consideration is involved.

In the present study, a method for the calculation of kinetic parameters using original or known programs for the package adapted for an IBM PC/AT is proposed. In our case, the degree of substance conversion is expressed through the loss of substance mass in the following manner:

$$\alpha = \frac{W_o - W}{W_o - W_K} \tag{6}$$

where W=substance mass at the instant of time t, W_o=substance mass at the start of the decomposition process, and W_K=substance mass at the end of the decomposition process, i.e. the solid residue.

In this case, Eq. (3) assumes the following form:

$$\begin{aligned} W(T) &= W_K + (W_o - W_K)\left[1 - \frac{E(1-n)}{RT_o} I(x)\right]^{1/(1-n)}; \quad n \neq 1 \\ W(T) &= W_K + (W_o - W_K)\exp\left[-\frac{E}{RT_o} I(x)\right]; \quad n = 1 \end{aligned} \tag{7}$$

Here

$$I(x) = \int_{x_o}^{x} \frac{e^{\xi} d\xi}{(S - \xi)^2}$$

where the following designations are introduced to make the computer calculations more convenient:

$$x = S - \frac{E}{RT}, \quad x_o = S - \frac{E}{RT_o}, \quad S = \ln\left(Z\frac{T_o}{\beta}\right)$$

In the case of (5), the formulae for $\alpha(T)$ are brought into the form:

$$\begin{aligned} W(T) &= W_K + (W_o - W_K)\left[1 - \frac{RT_o(1-n)}{E}(e^x - e^{x_o})\right]^{1/(1-n)}; \quad n \neq 1 \\ W(T) &= W_K + (W_o - W_K)\exp\left[-\frac{RT_o}{E}(e^x - e^{x_o})\right]; \quad n = 1 \end{aligned} \tag{8}$$

Equations (7) and (8) describe the kinetics of a process occurring in one stage, i.e. having one inflection point in the thermogravimetric curve, where the rate of decomposition of the substance is maximum.

The thermogravimetric curve of the decomposition process clearly indicated two independent processes, shifted in temperature relative to each other. Accordingly, the following model is proposed for two independent processes, having their own kinetic parameters over the individual ranges of decomposition.

Let us employ the following notations:

E_1, S_1, n_1=kinetic parameters of the first process;
E_2, S_2, n_2=kinetic parameters of the second process;
W_{oi}=initial mass of component i;
W_{Ki}=final mass of component i (i=1, 2).

$$\alpha_i = \frac{W_{oi} - W_i}{W_{oi} - W_{Ki}} \tag{9}$$

The unknown variables W_{o1}, W_{K1} and W_{o2} satisfy the following equations:

$$W_o = W_{o1} + W_{o2}, \; W_K = W_{K1} + W_{K2}$$

where W_o and W_K are known. Thus, for a two-stage process we have eight unknowns to be determined E_1, E_2, n_1, n_2, S_1, S_2, W_{o1} and W_{K1}.

Integration of the equations, similarly as for (1), with respect to α_1 and α_2 results in the following equations for $W_i(T)$:

$$\begin{aligned} W_i(T) &= W_{Ki} + (W_{oi} - W_{Ki})\left[1 - \frac{E_i(1-n_i)}{RT_o}I_i(x_i)\right]^{1/(1-n_i)}; \quad n_i \neq 1 \\ W(T_i) &= W_{Ki} + (W_{oi} - W_{Ki})\exp\left[1 - \frac{E_i}{RT_o}I_i(x_i)\right]; \quad n_i = 1 \end{aligned} \tag{10}$$

where

$$I_i(x) = \int_{x_{oi}}^{x_i} \frac{e^{\xi} d\xi}{(S - \xi)^2}$$

$$x_i = S_i - \frac{E_i}{RT}, \quad x_{oi} = S_i - \frac{E_i}{RT_o}, \quad i = 1, 2$$

In the case of approximate integration, derived from introduction of the factor T_o^2/T^2 on the right-hand side of Eq. (4), we have:

$$W_i(T) = W_{Ki} + (W_{oi} - W_{Ki})\left[1 - \frac{RT_o(1 - n_i)}{E_i}(e^{x_i} - e^{x_{oi}})\right]^{1/(1-n_i)}; \quad n_i \neq 1$$

$$W_i(T) = W_{Ki} + (W_{oi} - W_{Ki}) \exp\left[-\frac{RT_o}{E_i}(e^{x_i} - e^{x_{oi}})\right]; \quad n_i = 1 \qquad (11)$$

The curve of the temperature dependence of mass is estimated here from the equation $W(T) = W_1(T) + W_2(T)$. In calculations of the chosen mathematical model parameters (E, S and n) in the first case, and E_1, E_2, S_1, S_2, n_1, n_2, W_{o1} and W_{K1} in the second. We followed a method of parameter identification con-

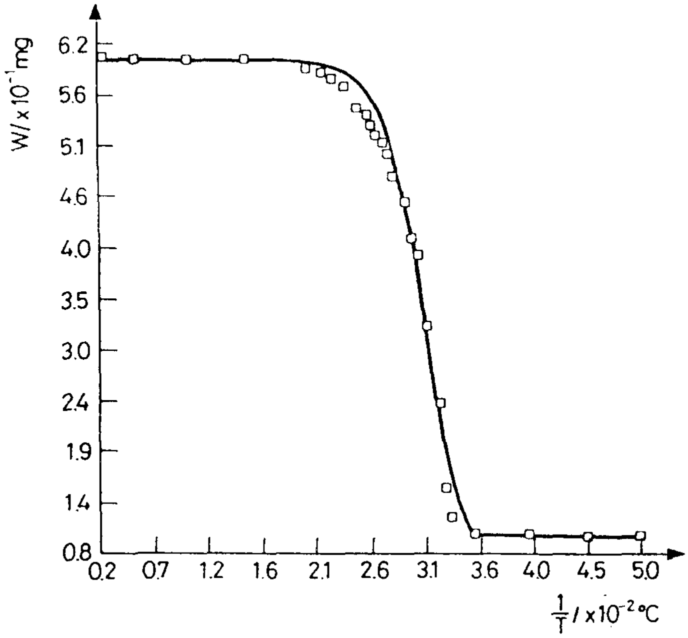


Fig. 1 3,3',5,5'-tetra-tert-butyl-4,4'-hydroxybiphenyl, method 1

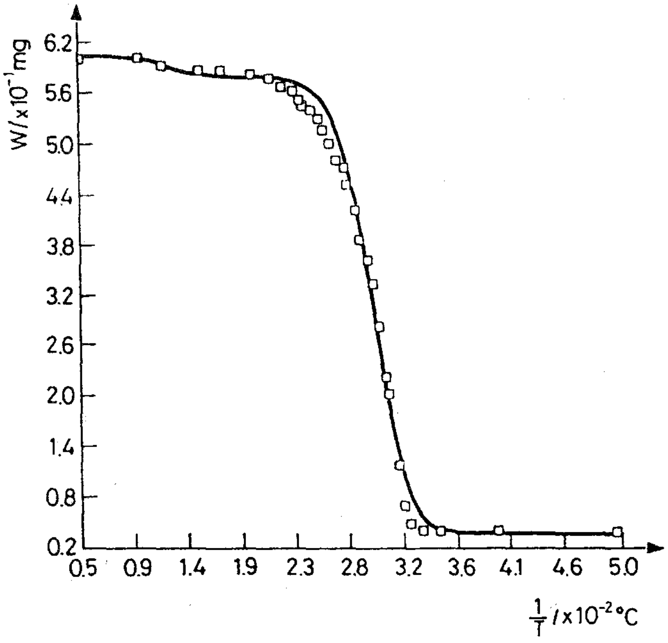


Fig. 2 Di-(3,5-di-tert-butyl-4-hydroxyphenyl)-methane, method 3

sisting in selection of the parameters providing the closest fit of the curve $W(T)$, represented by model (7), (8) or (11), to the curve $W_e(T)$, resulting from experiment. This can be performed by minimizing the following square function:

$$F = \sum_{i=1}^{N} [W(T_i) - W_e(T_i)]^2 \qquad (12)$$

representing the sum of the squares of the distances between functions $W(T)$ and $W_e(T)$ *at* N given points T_i, $i=1,2, \ldots, N$. Similar calculations demand the applications of a method of search for a minimum in the variable function.

This is achieved with the software package THERMOGRAPH. This package involves the following programs: graphical representation of the curves specified by the experimental points and formulae (7), (8) and (11); spline approximation; and calculation of definite integrals and optimization. The program package for graphical representation of the curves with a menu system considerably facilitates analysis of the obtained experimental data and functions modelling thermodegradation. The software package THERMOGRAPH reads out a table of experimental data, represented as a specially established file, as data, or a user introduces values of experimental points from a keyboard. The menu system also allows selection of mathematical model (7), (8) or (11) and

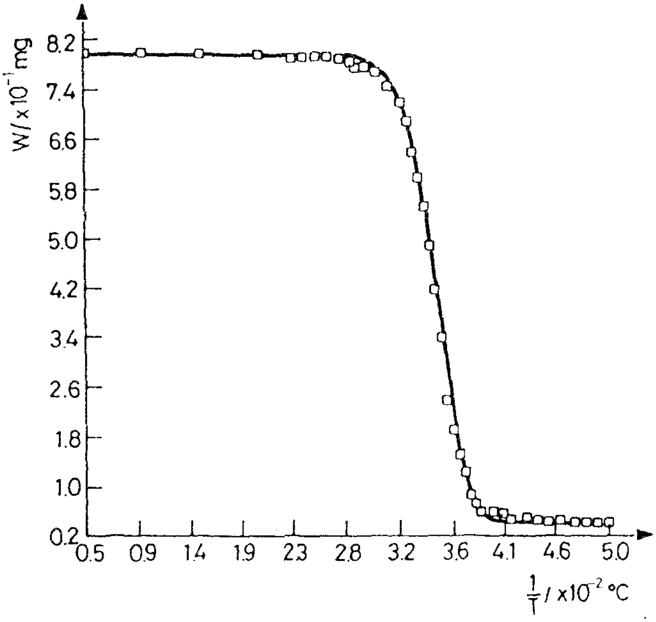


Fig. 3 2-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid-2,2'-thiobisethanol-diester, method 2

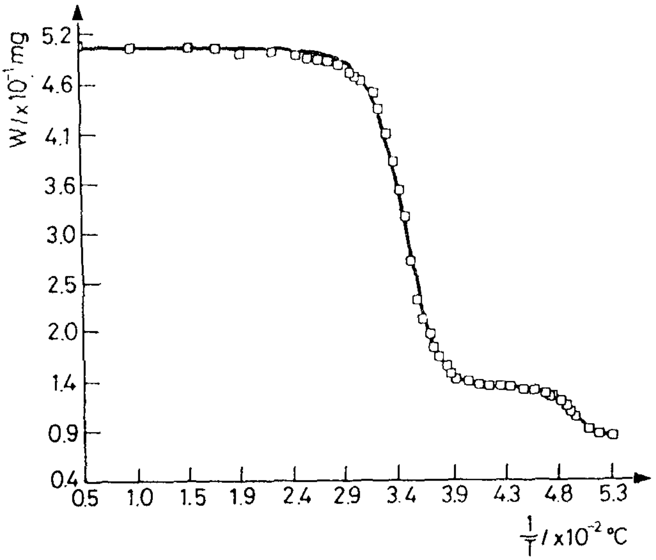


Fig. 4 Tris-(3,5-di-tert-butyl-4-hydroxyphenyl)-phosphate, method 3

the start of the program of optimization of function (12) for corresponding parameter identification. Further, the package for the graphic representation of

Table 1 Kinetic parameters of phenol stabilizers

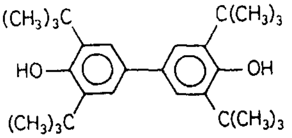
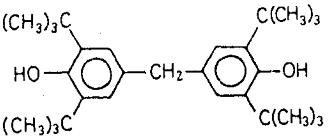
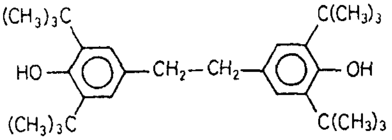
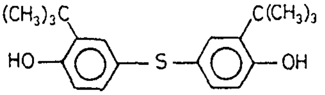
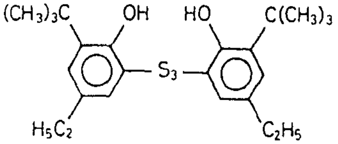
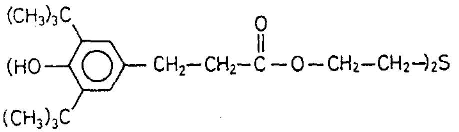
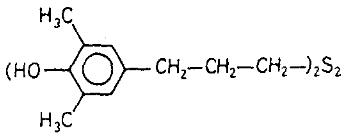
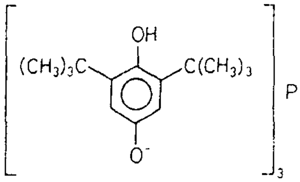
N	Compound	Formula	*E*/kJ mol^{-1}	*Z*/s^{-1}	*n*
1	3,3',5,5'-Tetra-tert-butyl-4,4'-hydroxybiphenyl		128.4	$3.0\cdot 10^{11}$	1.0
2	Di-(3,5-di-tert-butyl-4-hydroxyphenyl)-methane		151.6 132.4	$2.3\cdot 10^{19}$ $9.1\cdot 10^{11}$	2.9 1.0
3	Bis-1,2-(3,5-di-tert-butyl-4-hydroxyphenyl) ethane		208.0	$7.8\cdot 10^{18}$	1.0
4	Di-(3-tert-butyl-4-hydroxyphenyl) sulfide		179.5	$1.1\cdot 10^{16}$	2.0
5	Bis-(3-ethyl-5-tert-butyl-6-hydroxyphenyl)-trisulfide		172.9	$9.0\cdot 10^{16}$	3.9
6	2-(3,4-Di-tert-butyl-4-hydroxyphenyl)propionic acid-2,2'-thiobisethanol-diester		212.6	$8.3\cdot 10^{17}$	1.5
7	Di-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propyl] disulfide		142.7 239.9	$2.4\cdot 10^{13}$ $4.7\cdot 10^{18}$	1.0 2.5

Table 1 Continued

N	Compound	Formula	E/kJ mol^{-1}	Z/s^{-1}	n
8	Tris-(3,5-di-tert-butyl-4-hydroxyphenyl) phosphate		169.1 292.6	$1.6 \cdot 10^{14}$ $1.4 \cdot 10^{20}$	1.0 1.0

curves allows viewing of the obtained curve together with the curve based on the experimental data on the display, for visual evaluation of their agreement and hence the quality of the chosen model.

The program INTERMIT for definite integral calculation by the Hermite interpolation method [17] was applied when employing formula (7). Kinetic parameters for each experiment were calculated by using both models (7) and (8) based on function (12) minimization; for this purpose, the program POISK was used to search for the minimum in the variable function [18].

Modelling of experimental curves with two inflection points is more adequate for functions derived from formulae (11).

Listings from the display with theoretical curve images resulting from approximation to the experimental points of analysis for some stabilizers are exemplified in Figs 1–4. The agreement of the theoretical curve with the experimental points in the Figures verifies the validity of the chosen model. The results of kinetic parameter (E, Z and n) calculation are tabulated. As the magnitude of the reaction order is equal to unity, the decomposition on fusion may be assumed to proceed monomolecularly. The Table lists parameter n equal to 2, 3 and even more. This suggests a complex character of disintegration, and it is likely that several processes proceed concurrently.

Conclusions

The kinetic parameters E, Z and n for the thermodegradation of some phenol stabilizers have been calculated with the new software package THERMOGRAPH. The magnitudes of E and Z provide an idea of the enthalpy and entropy contributions to the kinetic tolerance of these stabilizers. The package can be applied for kinetic calculations relating to the thermodegradation of various organic compounds.

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