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# THERMAL TRANSFORMATION OF SOLID ORGANIC COMPOUNDS

## I. KINETIC EQUATIONS FOR THE THERMAL DECOMPOSITION OF CRYSTALLINE MALONIC ACID

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The thermal decomposition of malonic acid was investigated with a derivatograph. Values of activation energy, frequency factor and reaction order were determined from thermal decomposition curves employing different calculation methods. Equations derived for the calculation of kinetic data of inorganic thermal reactions were also found to be suitable in the case of organic reactions. Convenient methods were developed for the calculation of the activation energy, using the DTG curve.

The importance of the science dealing with chemical reactions occurring in inorganic solids on heating has grown steadily in the last decade. Several industrial processes are based on such reactions. The general trend to control them has resulted in extensive studies of their mechanisms, and kinetic and thermodynamic characters [1].

In general, transformations of organic solids are not considered very important and only few data are available [2] e.g. for ammonium mucate [3] and L-glutamic acid [4] which form well-defined intermediates during their pyrolysis.

In spite of the fact that the number of described organic thermal reactions is small, they can afford new preparative possibilities. We have examined thermal transformations occurring in organic solids, and the mechanism and kinetics of such reactions, assuming that this will lead to further results.

During the last two decades a number of methods have been developed for studying the isothermal and non-isothermal decomposition of inorganic solids. Results with organic compounds are smaller in number, thus further investigation is required involving the solution of methodological problems.

Within the range of investigation of the non-isothermal decomposition of crystalline malonic acid, we deal with methodological problems such as the calculation of reaction kinetic data. Equations derived for the description of the thermal reactions of inorganic solids have been employed for this. Considering the possibilities offered by the derivatograph we attempted to simplify the equations.

By investigating simple reactions we tried to find an answer to the following questions:

*a)* Can the kinetic equations for inorganic solid-phase reactions be applied to organic substances?

*b)* In what manner can comparisons be made between the kinetic data for isothermal and non-isothermal thermal reactions?

## Characteristics of the thermal transformation of organic solids

The thermal reactions of solid-state organic and inorganic substances are essentially different due to the quantitative and qualitative differences in their atomic relations and in the characteristic cohesive forces acting between their crystals [2]. In general, the decomposition of organic substances is characterized by the formation of a liquid phase and gaseous decomposition products.

In the course of reaction kinetic measurements carried out under isothermal conditions no methodological differences are caused by liquefaction. In the evaluation of kinetic data, however, it is an important factor. For reactions occurring in both the liquid and solid phase, the transformation rate is generally higher in the liquid phase, and lower energy input is required.

## Literature data for the thermal transformations of malonic acid

Malonic acid melts around 134°, and then decomposes [5] according to the equation:

$$HOOC-CH_2-COOH \longrightarrow CH_3COOH + CO_2$$

At the decomposition temperature both products are in the gaseous state. The process is relatively simple. The products formed during decomposition escape and their effect on the reaction may be neglected under suitable experimental conditions. The kinetics on the decomposition occurring under isothermal conditions in the solid and supercooled liquid states have been studied by Hinshelwood [6]. He assumed first order reactions in both cases. For kinetic calculations he measured the pressure of gas generated during decomposition, and plotted it as a function of time. He found activation energies of 60.4 kcal $mole^{-1}$ and 32.4 kcal $mole^{-1}$ for the solid state and liquid-state reactions, respectively.

## Kinetic methods for transformations under non-isothermal conditions

The kinetic calculation methods based on thermoanalytical measurements can be divided into three main groups:

1. Methods based on thermogravimetric (TG) curves.
2. Methods based on differential thermoanalytical (DTA) curves.
3. Methods based on the modifications of thermoanalytical curves due to different heating rates.

The literature also mentions combining the fundamental methods. We attempted to investigate the kinetic character of thermal reactions of organic solids with one of the above methods, relying on the fact that pressure vs. time functions, characterizing the isothermal decomposition of inorganic substances, may be conveniently applied to the transformation of organic compounds [2].

## Equations employed for the kinetic description of the decomposition of malonic acid

From the methods based on the TG curve we chose the Horovitz–Metzger equation [7]. For monomolecular reactions, the following relationship is valid:

$$\ln\ln \frac{W_0}{W} = \frac{E_A}{RT_S^2}\,\Theta \tag{1}$$

where $E_A$ = activation energy
$R$ = gas constant
$W_0$ = initial weight of substance
$W$ = residual weight of substance
$\Theta = T - T_S$
$T_S$ = reference temperature at which $\frac{W}{W_0} = \frac{1}{e}$
$T$ = absolute temperature.

If $\ln\ln \frac{W_0}{W}$ is plotted against $\Theta$, a straight line is obtained its slope $\mathrm{tg}\,\alpha = \frac{E_A}{RT_S^2}$, from which the value of $E_A$ may be calculated.

From $T_S$ and $E_A$ knowing the heating rate ($\phi$), the frequency factor of the Arrhenius equation may be calculated from the equation:

$$Z = \phi \frac{E_A}{RT_S^2} \cdot \exp \frac{E_A}{RT_S} \tag{2}$$

where $Z$ = frequency factor

$\phi$ = heating rate = $\frac{\mathrm{d}T}{\mathrm{d}t}$ (°C $\mathrm{min}^{-1}$).

From the different equations based on transformations occurring at different heating rates we selected the equations of Kissinger [8], and the method of Wiedemann and co-workers [9].

Kissinger based his kinetic equation for the calculation of $E_A$ on the fact that the peak temperature ($T_m$) of the DTA curve is dependent on the heating rate ($\phi$). The relationship is given by:

$$\frac{\mathrm{d}\ln\frac{\phi}{T_m^2}}{\mathrm{d}\,T_m^{-1}} = -\frac{E_A}{R}. \tag{3}$$

Plotting $\ln\frac{\Phi}{T_m^2}$ in the function of $T_m^{-1}$ a straight line is obtained of slope $-\frac{E_A}{R}$. From this, the value of $E_A$ can be calculated.

Wiedemann and co-workers started from the Arrhenius equation:

$$k = Z \cdot \exp\frac{E_A}{RT} \tag{4}$$

where $k$ = velocity constant.

They state that the relationship is also true in the form:

$$k = f(\alpha)\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{5}$$

For a decomposition reaction of the $n$th order, $f(\alpha)$ is equal to $(1-\alpha)^n$. The reaction factor $\alpha$ is proportional to the weight loss of the sample, in the case of complete decomposition $\alpha$ being unity. The term $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ represents the decomposition rate of the sample; its value may be determined by the slope of the TG curve at individual $\alpha$ values. If $\alpha$ is inserted as a parameter $\left(\text{e.g. } \alpha = \frac{1}{2}\right)$, from the relationship for $k$ we obtain that the logarithm of $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ is a linear function of the reciprocal of the absolute temperature; thus if $\log\frac{\mathrm{d}\alpha}{\mathrm{d}t}$, obtained from the TG curve recorded with different heating rates, is plotted as a function of the reciprocal of the corresponding absolute temperature, a straight line is obtained of slope $\mathrm{tg}\,\beta$. The activation energy may be calculated from $E_A = 2.3\,R \cdot \mathrm{tg}\,\beta$.

The equations chosen for the calculation of kinetic decomposition data require a knowledge of the reaction order. This was calculated using the Kissinger method [8] based on the symmetry of the DTA curve.

Kissinger proposed the employment of the correlation between the reaction order ($n$) and the form of the DTA curve for the determination of $n$. With decreasing $n$, the asymmetry of the curve increases, assuming measurements under identical conditions. For its numerical characterization he introduced the shape index ($S$). Starting from the analytical expression of $S$,

$$S = \left| \frac{\left(\frac{d^2x}{dt^2}\right)_1}{\left(\frac{d^2x}{dt^2}\right)_2} \right| \tag{6}$$

he established theoretically the following correlation between $S$ and $n$:

$$S = 0.63 \cdot n^2, \text{ from which } n = 1.26\sqrt{S}. \tag{7}$$

## Attempts to simplify the Wiedemann equation

In order to reduce the Wiedemann equation we started from the fact that the DTG curve is characteristic of the rate of loss of weight of the sample [10]. The derivatograph produces the DTG curve instrumentally, but its graphical construction is also possible. In this case we plot slopes of the tangent drawn to individual points of the TG curve. It can be seen that in the Wiedemann method the step involving the calculation of the slope at point $\alpha = \frac{1}{2}$ on the TG curve corresponds to the reading on the DTG curve at the same $\alpha$ value; thus at this poin

$$\frac{d\alpha}{dt} = \frac{dm}{dt}.$$

Thus the term $\frac{d\alpha}{dt}$, the determination of which is rather difficult and inaccurate, may be substituted by the term $\frac{dm}{dt}$ and the equation becomes:

$$k = f(\alpha)\frac{dm}{dt}. \tag{8}$$

The numerical value of $\frac{dm}{dt}$ can be obtained precisely by a simple reading from the calibrated DTG curve. For the calculation of the activation energy, $\log \frac{dm}{dt}$ values for identical points on the DTG curves at different heating rates are plotted against the reciprocal of the corresponding absolute temperatures. From the slope (tg $\beta$) of the straight line obtained, the value of $E_A$ can be calculated.

## Experimental conditions

Measurements were made with a MOM Paulik–Paulik–Erdey derivatograph. The DTA and DTG galvanometers of the instrument were calibrated as in [11], permitting the determination of temperature differences between the sample and the inert material, as well as the numerical value of $\frac{dm}{dt}$, i.e. the decomposition rate. Recordings were made at different heating rates in argon of 99.96 per cent purity and in air. Samples of about 50, 100, 200 and 500 mg were studied using platinum crucibles or a poly-plate sample holder [12].

Experimental conditions are summarized in Table 1.

Table 1

Experimental conditions

| No. | Weight of sample (mg) | Atmosphere | Sample holder | Heating rate °C min$^{-1}$ |
|---|---|---|---|---|
| 1 | 48.0 | Ar | crucible | 0.8 |
| 2 | 48.5 | Ar | poly-plate holder | 1.0 |
| 3 | 99.0 | Ar | ,, | 2.9 |
| 4 | 465.0 | Ar | ,, | 3.0 |
| 5 | 195.0 | Ar | ,, | 3.3 |
| 6 | 94.0 | air | crucible | 4.0 |
| 7 | 191.0 | air | poly-plate holder | 6.1 |
| 8 | 450.0 | Ar | ,, | 7.0 |
| 9 | 453.0 | Ar | ,, | 7.3 |
| 10 | 94.6 | Ar | ,, | 7.6 |
| 11 | 183.0 | Ar | crucible | 8.0 |
| 12 | 192.0 | air | ,, | 7.9 |
| 13 | 188.0 | air | ,, | 8.4 |

## Experimental results

The thermal decomposition curves of malonic acid produced under different experimental conditions are very similar. Consequently, in Fig. 1 only one curve (No. 3) is given.

The first step on heating involves a modification of the crystal structure of malonic acid. This occurs between 80 and 100°, DTA peak temperature 88° (1 in the Figure). Melting is indicated on the DTA curve by a peak at 133° [2]. Decomposition starts after melting and takes place between 127 and 187°, reaching its maximum rate at 165° (DTG maximum). Our results are in agreement with the data published earlier by Gál and co-workers [5].

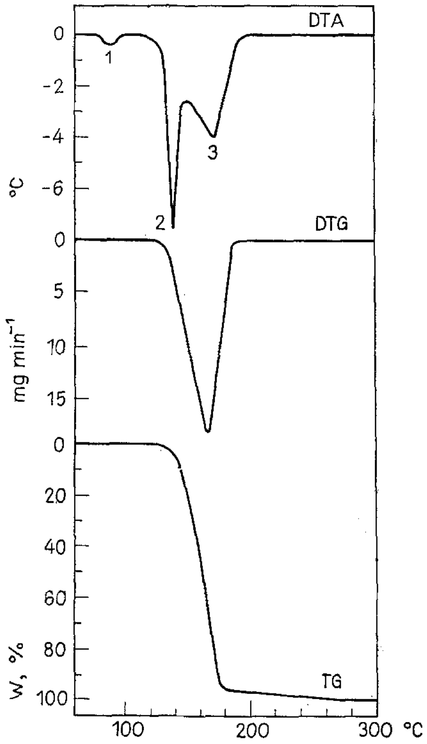

Fig. 1. Thermal decomposition of malonic acid

## Calculation of the kinetics of the decomposition reaction

*Using the Horovitz–Metzger method* [Eq. (1)], as a first step we calculated the values of $E_A$ from the TG curve of the derivatograms. With a knowledge of $E_A$, values of the frequency factor $Z$ in the Arrhenius equation were obtained from Eq. (2). Values of $E_A$ and $Z$ are given in Table 2.

The straight line obtained from the DTA curves produced at different heating rates using *the equation of Kissinger* is shown in Fig. 2; from this the slope calculated by the least squares method and $E_A$ are $-6.78$ and 31.2 kcal mole$^{-1}$, respectively.

*In calculating the $E_A$ value by the Wiedemann method* [Eq. (5)], we also started from the thermal curves recorded at different heating rates. An essential part

Table 2

Values of $E_A$ and $Z$ calculated by means of Eqs (1) and (2)

| No. | $E_A$ [kcal mole$^{-1}$] | $Z$ [sec$^{-1}$] |
|---|---|---|
| 1 | 37.9 | $3\times10^{18}$ |
| 2 | 39.2 | $9.6\times10^{18}$ |
| 3 | 40.4 | $6.5\times10^{19}$ |
| 4 | 40.9 | $1.2\times10^{20}$ |
| 5 | 40.6 | $6.7\times10^{19}$ |
| 6 | 30.9 | $8.9\times10^{14}$ |
| 7 | 43.0 | $1.2\times10^{21}$ |
| 8 | 40.0 | $2.4\times10^{19}$ |
| 9 | 40.2 | $7.5\times10^{19}$ |
| 10 | 36.6 | $9.6\times10^{17}$ |
| 11 | 35.2 | $1.4\times10^{17}$ |

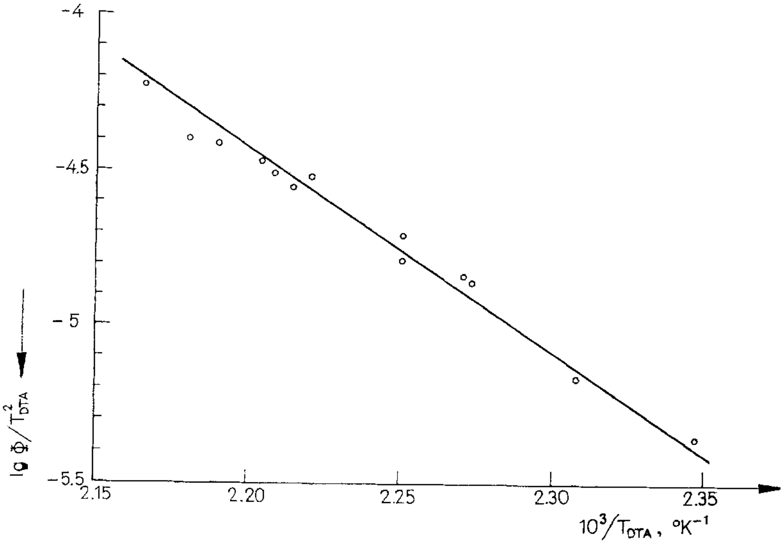

Fig. 2. The straight line obtained by means of Eq. (3)

of the numerical calculations involves the plotting of the slope relating to the value of $\alpha = 1/2$. As a first step, the tangent must be drawn at the point marked on the TG curve, as inaccurate drawing may result in miscalculation of the slope value. Using the conception of Hoare [13], a home-made "slope ruler" was constructed which permits the slopes to be drawn more easily and with greater precision. Polished plexiglass rods of 6 mm and 20 mm diameter were fixed into a transparent ruler (Fig. 3) such that the axes of the rods were perpendicular to the edge of the ruler.

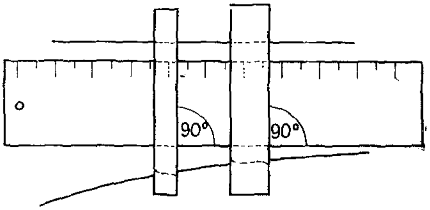

Fig. 3. Sketch of "slope ruler"

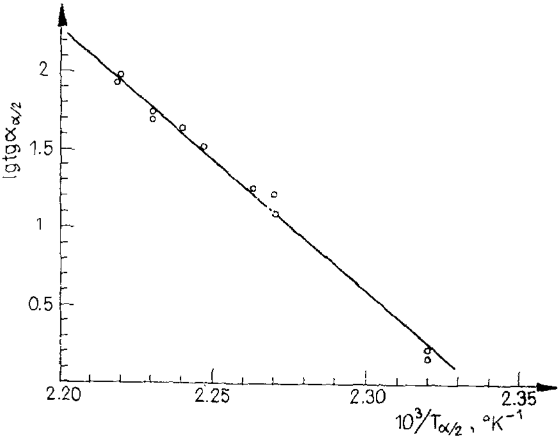

Fig. 4. The straight line obtained by means of Eq. (5)

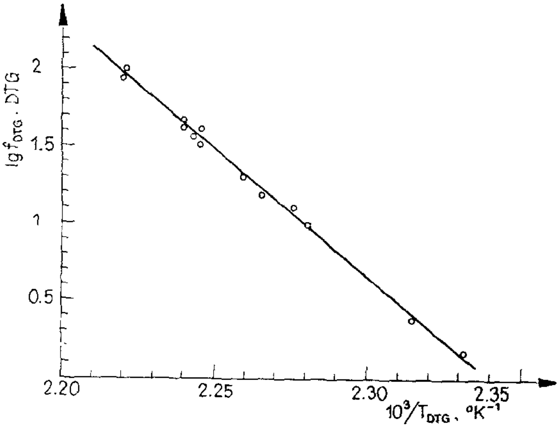

Fig. 5. The straight line obtained by means of Eq. (6)

The slope is drawn as follows: the axis of the rod is placed at the designated point on the TG curve and moved until, looking through the rod, a continuous curve is obtained. In this case the edge of the ruler marks the tangent relating to the point of the curve in question.

The straight line obtained by plotting the data is given in Fig. 4; its slope is 8.7, and $E_A$ is 40.0 kcal mole$^{-1}$.

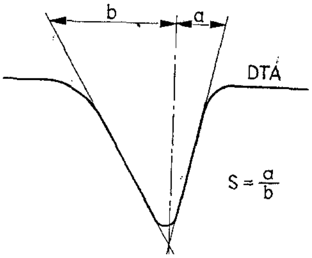

Fig. 6. The construction of the shape index from the DTA curve

*Calculation of* $E_A$ *from the calibrated DTG curve* [simplified Wiedemann method, Eq. (8)] consists of the following operations for each recording:

*a)* Reading in mm of the maximum deviation of the DTG curve; its multiplication by the appropriate calibration factor $\left(\text{value of } \frac{dm}{dt}\right)$.

*b)* Reading of the peak temperature of the DTG curve ($T_{DTG}$).

Table 3

The values of reaction order

| No. | $n_{DTA}$ |
|---|---|
| 1 | 0.77 |
| 2 | 0.84 |
| 3 | 0.77 |
| 4 | 0.75 |
| 5 | 0.74 |
| 6 | 0.57 |
| 7 | 0.67 |
| 8 | 0.69 |
| 9 | 0.72 |
| 10 | 0.73 |
| 11 | 0.84 |
| 12 | 0.74 |
| 13 | 0.68 |

*c)* Plotting $\log \frac{\mathrm{d}m}{\mathrm{d}t}$ against $\frac{1}{T_{\mathrm{DTG}}}$ which results in a straight line (Fig. 5).

*d)* Obtaining the slope of the straight line, from which

$$E_A = 2.3\ R \cdot \mathrm{tg}\,\beta = 39.8\ \text{kcal mole}^{-1}.$$

*Calculation of the reaction order (n) by the Kissinger shape index method* consists in constructing the shape index $S$ according to Fig. 6, and calculating the reaction order $n$ from the equation $n = 1.26\sqrt{\frac{a}{b}}$. Values of $n$ calculated by means of the DTA curves produced at different heating rates are given in Table 3.

## Evaluation of the experimental results

Malonic acid was chosen as the first model for the kinetic investigation of solid organic reactions because the mechanism of its thermal decomposition and the kinetic characteristics of the reaction under isothermal conditions are known [6]. The decomposition of malonic acid is of the type

$$A_{\mathrm{solid}} \rightarrow [A_{\mathrm{liquid}}] \rightarrow B_{\mathrm{gas}} + C_{\mathrm{gas}}.$$

For the kinetic description of such reactions, Horovitz and Metzger have developed calculation methods [7] from which, in principle, Eqs (1) and (2) are applicable to the thermal reactions of malonic acid. From the kinetic data it may be decided whether or not other kinetic equations may be applied, and in addition isothermal and non-isothermal measurement data may be compared.

Kinetic data of the decomposition of malonic acid obtained by measurements under non-isothermal conditions and calculated by different methods are given in Table 4.

Table 4

Kinetic data for the decomposition of malonic acid calculated by different methods

| | Horovitz–Metzger | Wiedemann | Kissinger | Based on DTG | Hinshelwood** |
|---|---|---|---|---|---|
| $E_A$ [kcal mole$^{-1}$] | 40* | 40.0 | 31.2 | 39.8 | 32.4 |
| $Z$ [sec$^{-1}$] | $10^{19\pm1}$* | | | | $10^{13.6}$ |
| $n$ | | | 0.73* | | 1 |

* Arithmetical mean values
** Measured under isothermal conditions

The thermal decomposition curves of malonic acid obtained derivatographically proved to be suitable for kinetic calculations. Values of $E_A$ calculated by different methods are higher compared with isothermal measurement results, with the exception of those from the Kissinger method [8]. Deviations may be attributed to different measurement conditions in the first place, in consequence of which different calculation methods were employed.

In the case of non-isothermal conditions the value of $Z$ is five orders of magnitude higher. Its magnitude is strongly influenced by the value of $E_A$, as clearly shown in Eq. (2). On the other hand, several authors have stated [2] that the value of $Z$ may change considerably.

Our data obtained for the reaction order calculated by the Kissinger DTA shape index method differ by 27 per cent from the isothermal measurement result. The calculated values of $n$ are independent of the heating rate within the accuracy of the calculation method.

Application of the Horovitz – Metzger equations (1, 2) need one measurement only, but many numerical calculations. One measurement only does not give reliable enough results, and several measurements are rather time-consuming.

The methods of Wiedemann and Kissinger, which permit the calculation of $E_A$ require more measurements but less numerical calculation. The accuracy of the data is strongly influenced by temperature readings. They have the advantage that the reaction mechanism need not be known.

Calculation of the reaction order by the Kissinger shape-index method from the DTA curve has not proved to be reliable.

With the calibrated DTG curve the reduced Wiedemann equation (6) does lead to reliable results. The DTG curve eliminates the difficult and uncertain construction of weight loss rates and reduces numerical calculation. The method seems to be convenient for the calculation of activation energy of transformations involving weight changes.

It can be seen from kinetic data calculated from measurements carried out under different experimental conditions that true values can only be obtained from curves produced under identical conditions. Results are greatly influenced by the shape of the sample holder.

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Résumé — On a étudié la décomposition thermique de l'acide malonique à l'aide du "Derivatograph". On a déterminé les valeurs de l'énergie d'activation, du facteur de fréquence et de l'ordre de la réaction en se rapportant aux courbes de décomposition thermique et en utilisant différentes méthodes de calcul. On a trouvé que les équations utilisées pour le calcul des données cinétiques dans le cas des réactions de la chimie minérale s'appliquent également aux réactions de la chimie organique. En utilisant la courbe de thermogravimétrie dérivée, on a développé des méthodes appropriées au calcul de l'énergie d'activation et de l'ordre de la réaction, avec une bonne applicabilité aux courbes obtenues à l'aide du "Derivatograph".

Zusammenfassung — Es wurde die thermische Zersetzung der Malonsäure derivatographisch untersucht. Aus den thermischen Zersetzungskurven konnten durch verschiedene Methoden die Werte der Aktivierungsenergie, des Frequenzfaktors und die Reaktionsordnung ermittelt werden. Die zur Berechnung der kinetischen Daten von anorganischen thermischen Reaktionen dienenden Gleichungen sind auch auf organische Reaktionen anwendbar. Es wurde eine Methode zur Berechnung der Aktivierungsenergie und der Reaktionsordnung, unter Verwendung der derivierten thermogravimetrischen Kurve entwickelt, die sich bei den derivatographischen Kurven ebenfalls gut bewährte.

Резюме — С помощью дериватографа исследован термораспад малоновой кислоты. На основании кривой термораспада при использовании различных методов расчета, определены величина энергии активации, фактор частоты и порядок реакции. Уравнения, выведенные для расчета кинетических данных неорганических термических реакций подходят и в случае органических реакций. С применением ДТА-кривой разработан метод, который можно использовать для расчета энергии активации и порядка реакции.