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KINETIC ANALYSIS OF ISOTHERMAL, NON-ISOTHERMAL AND CATALYSED THERMAL DECOMPOSITION OF MALONIC ACID

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A comparative study of the isothermal and non-isothermal decompositions of malonic acid has been carried out using the gasometric technique at atmospheric pressure. Under isothermal conditions, the results indicate two different mechanisms. At lower operating temperatures the decomposition process is governed by first-order kinetics, while at higher temperatures it is controlled by the random nucleation Erofeev equation. Analysis of the non-isothermal TG curves proved the advantageous use of this technique. It provides quick and valid information about the thermal decomposition kinetics of malonic acid, both in the pure state and when catalysed by solid 12-molybdophosphoric acid and its bismuth salts. Via the applicability of a non-isothermal kinetic equation, it was demonstrated that the factor causing the enhancement effect of these catalysts is mainly electronic in nature.

The kinetics of thermal decomposition of solids has attracted the interest of investigators under both isothermal and non-isothermal conditions. It has been reported [1, 2] that the kinetic analysis of thermogravimetric data obtained under isothermal conditions is preferable, with the integral kinetic equation

$$g(\alpha) = Kt$$

where α is the fraction of solid decomposed after time t, K is the constant rate, which is related with temperature by the Arrhenius equation

$$K = Ae^{-E/RT}$$

and $g(\alpha)$ is a function depending on the decomposition mechanism. On the other hand, several examples have demonstrated [3, 4a] that non-isothermal kinetic measurements may give information about the kinetics of a decomposition process that is equivalent to the information resulting from isothermal studies, especially when the latter demand additional experimental data associated with the unwanted decomposition of the reactant during the heating period. In such a case, there are advantages to using the non-isothermal method, which supplies the fraction decomposed and the corresponding sample temperature throughout the studied process, as a property sufficiently sensitive to represent the course of the decomposition [4b].

In the present paper, we attempt first a comparative kinetic analysis of thermogravimetric data on malonic acid decomposition under isothermal and non-isothermal conditions. Next, we examine earlier conclusions relating to this thermal decomposition [5] with bifunctional heteropoly compounds as solid catalysts [6].

Experimental

Reagent grade chemicals were used. The decomposition of malonic acid at atmospheric pressure was followed by using the gasometric technique [7]. A trap was inserted to allow measurement only of the CO_2 gas evolved during the thermal decomposition. The heating rate was 7 deg/min. A Gallenkamp NiCr/NiAl BS 4937 temperature controller was used in the isothermal decomposition kinetics studies. The fraction decomposed (α), or the ratio between the volume of evolved CO_2 and the total volume evolved at complete decomposition, was represented as a function of time or temperature for the iso- and non-isothermal conditions, respectively. The total volume of CO_2 that could be liberated was checked theoretically from the known amount of malonic acid, and was finally corrected to room temperature to correspond to $\alpha = 1$.

Catalysts were prepared and used in the catalytic thermal decomposition of malonic acid as described previously [6, 8].

Results and discussion

Figure 1 shows the α *vs.* t curves for the isothermal decomposition of malonic acid. These curves, obtained in the temperature range 418–521 K, reveal that an initial period sets in when the sample has reached the furnace temperature. The isothermal data for the main process beginning after this initial period were analysed according to the various kinetic equations [9] given in Table 1.

The results showed that the first-order kinetic equation (F_1) gives the best fit to the data obtained at lower temperatures, while at higher operating temperatures the random nucleation Erôfeev equation (A_3) appears to be the most valid to yield good straight lines (Fig. 2). Application of the Arrhenius equation (Eq. (1)) provides different values for the kinetic parameters, depending on the operating temperatures:

$$K = A \exp^{(-E_a/RT)} \qquad (1)$$

where K = decomposition rate, A = pre-exponential factor, and E_a = activation energy.

The obtained values (calculated by the least square method) are $E_a = 18.37 \pm 0.29$ Kcal mol^{-1} with $\ln A = 19.05 \pm 0.68$, and $E_a = 9.4 \pm 0.37$ Kcal mol^{-1} with $\ln A = 9.0 \pm 0.56$, at lower and higher operating temperatures, respectively.

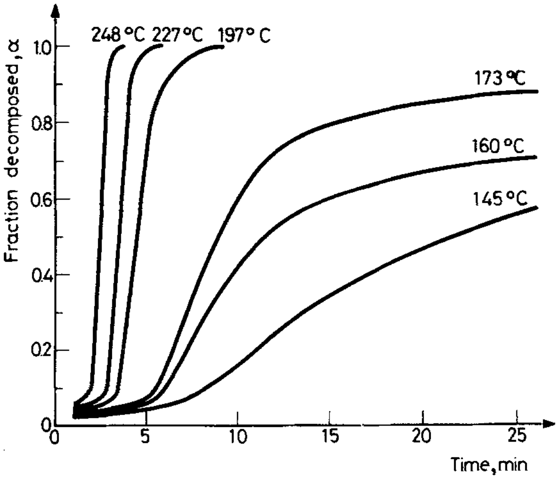

Fig. 1 α *vs.* t curves for the isothermal decomposition of malonic acid

Table 1 Kinetic equations examined in this work

Reaction model	$g(\alpha) = Kt$	Function symbol
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$\alpha+(1-\alpha)\ln(1-\alpha)$	D_2
Jander equation, three-dimensional diffusion	$\{1-(1-\alpha)^{1/3}\}^2$	D_3
Ginstling–Brounshtein equation, three-dimensional diffusion	$\left(1-\frac{2}{3}\alpha\right)-(1-\alpha)^{2/3}$	D_4
Two-dimensional phase boundary reaction	$\{1-(1-\alpha)^{1/2}\}$	R_2
Three-dimensional phase boundary reaction	$\{1-(1-\alpha)^{1/3}\}$	R_3
First-order kinetics	$-\ln(1-\alpha)$	F_1
Random nucleation: Avrami equation	$\{-\ln(1-\alpha)\}^{1/2}$	A_2
Random nucleation: Erofeev equation	$\{-\ln(1-\alpha)\}^{1/3}$	A_3

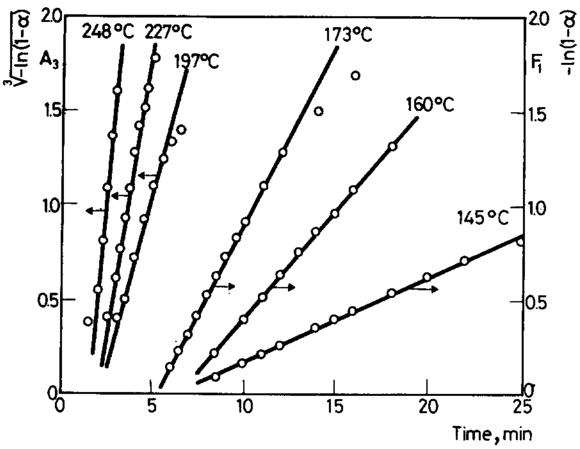

Fig. 2 Isothermal decomposition of malonic acid according to F_1 and A_3 mechanisms

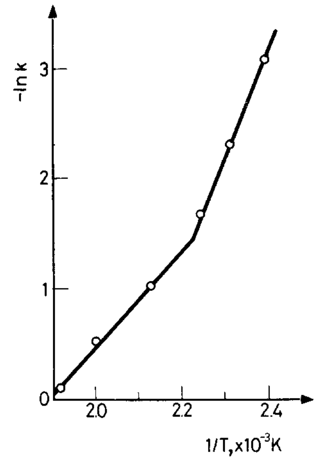

Fig. 3 Arrhenius plot for the isothermal decomposition of malonic acid

From the above findings, it appears that the isothermal data may lead to a wrong conclusion about the decomposition mechanism. This emerges from the observation that malonic acid decomposes according to the following equation [10]:

$$CH_2(COOH)_2 \rightarrow CO_2 + CH_3COOH \qquad (2)$$

which cannot be plausibly described by the nucleation mechanism. Therefore, we believe that the non-isothermal measurement may be recommended to give more reliable kinetic information during the entire decomposition process.

A series of characteristic non-isothermal curves for malonic acid decomposition are shown in Fig. 4. They were recorded at constant heating rate, constant particle size and constant shape of the sample holder; the only difference relates to the sample weight. This difference can be well seen in the case of the TG values, as a shift to higher temperature with increasing sample weight. Such an observation can be interpreted if we accept the physical concept that two processes take place in the sample [11]:

(i) heat transport towards the interior of the sample,

(ii) outward transport of products from the sample.

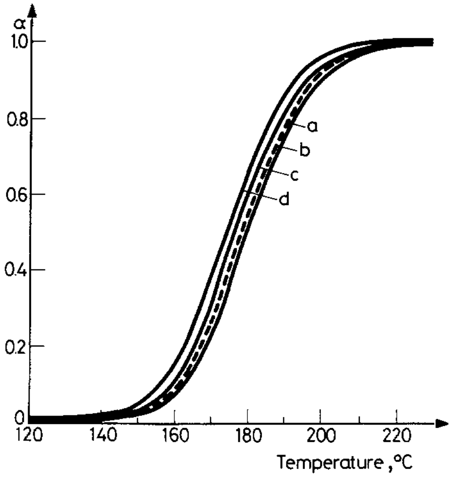

Fig. 4 α *vs.* temperature curves for the non-isothermal decomposition of malonic acid in weights of 300, 400, 200 and 100 mg (*a–d*, respectively)

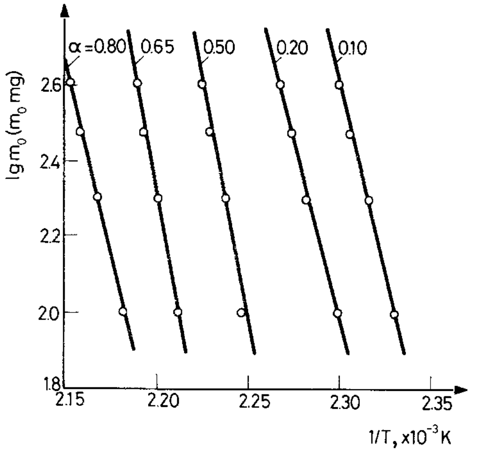

Fig. 5 Plots of $\log m_0$ *vs.* $1/T$ at fixed values of α

The liberation and diffusion of gaseous product (CO_2) is more hindered in larger samples than in smaller ones. This conception was checked by plotting log m_0 (m_0 is the initial mass in mg) *vs.* $1/T$ at a fixed value of α as obtaineed from Fig. 5. Straight lines were obtained at each value of α, in good agreement with the Pokol equation [12]

$$\log m_0 = (C - D/1 - B)1/T \qquad (3)$$

(C and D are constants)

From Eq. (3) two cases were distinguished: $B = 1$ when the decomposition reaction goes on the same time, and $B < 1$ when there is a moving reacting zone in the sample. The slopes of the straight lines in Fig. 5 show that B differs from 1, so the second case is the valid one. In this case, the rate depends mainly on the transport processes, and probably on the outward transport of CO_2 from the sample, as suggested earlier.

In order to evaluate the kinetic parameters from the non-isothermal TG curve, the following equation was used [12, 13]:

$$\ln \alpha - 2 \ln T = \ln \frac{AR}{E_a \beta} - E_a/RT \qquad (4)$$

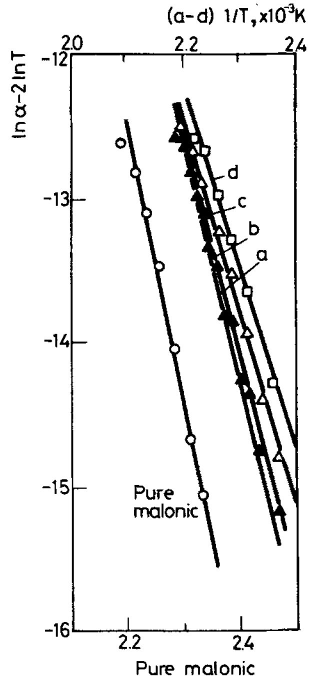

Fig. 6 (ln $\alpha - 2$ ln T)*vs.* $1/T$ for calculation of the E_a value from a single TG curve for pure malonic acid and for malonic acid mixed with 10% (*wt/wt*) catalyst. Catalysts used: H_3P, $Bi(H_2P)_3$, $Bi_2(HP)_3$ and BiP (*a–d*, respectively)

(where β is the heating rate and the other terms have their usual meanings). The activation energy value (E_a) and the pre-exponential factor (A) were determined from the fact that the slope of the straight line plot of ($\ln \alpha - 2 \ln T$) *vs.* the inverse of the absolute temperature is proportional to E_a, while the intercept is equal to $\ln AR/E_a\beta$. The values obtained were 35.03 ± 0.41 Kcal mol^{-1} and 2.75×10^{16} for E_a and A, respectively.

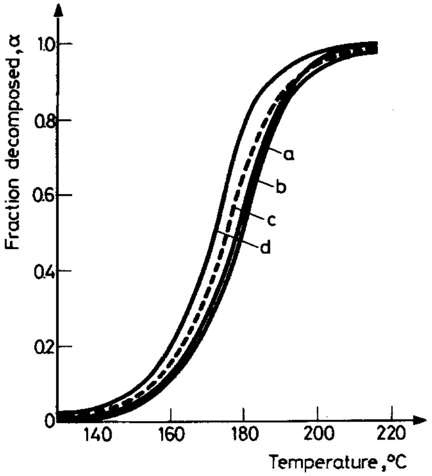

Fig. 7 TG curves characteristic of the catalysed thermal decomposition of malonic acid (symbols as in Fig. 6)

The applicability of the above equation proved the advantageous use of a non-isothermal TG curve to obtain quick and valid information about the kinetics of thermal decomposition of malonic acid. This was used to reveal the effectiveness of some catalysts in our decomposition process. Two factors are known to influence the homogeneous decomposition of malonic acid [14]: the presence of reducible cations and the concentration of H^+ ions in the medium. Therefore, it was of interest to examine the decomposition heterogeneously in the presence of a solid catalyst with a bifunctional nature (acidic and oxidizing). 12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}$) and its bismuth salts offer good examples of such catalysts.

The TG curves characteristic of these catalysed thermal decompositions (Fig. 7) demonstrated a significant effect on the decomposition process, which appears as a shift in the TG curves to lower temperatures. This shift increased in the following sequence: $BiP > Bi_2(HP)_3 > Bi(H_2P)_3 > H_3P$ (where P denotes $PMo_{12}O_{40}$). This situation leads to the concept that the factor responsible for the enhancement effect in this case is mainly electronic in nature (this concept finds support from the observed higher activity of the neutral catalyst BiP).

In order to relate this enhancement effect to a parameter indicative of the electrical property change of the various catalysts, it must be mentioned that the molybdenum is the active element in these catalysts and the electronic property changes with the electronegativity of its environment. Therefore, an estimate of the fractional charge on molybdenum, δ_{MO}, may suffice for our purpose [15]. The results showed that the enhancement effect, as detected from the shift in the TG curves to lower temperatures, runs parallel with the increase in δ_{Mo}, i.e. an increase in the electron affinity of molybdenum tends to enhance the decomposition process through the ease of electron-donation from the malonic acid molecule.

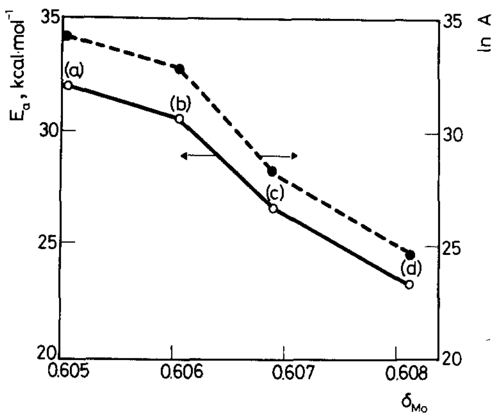

Fig. 8 Variation of E_a and ln A for the catalysed thermal decomposition of malonic acid with the partial charge value on molybdenum in these catalysts (δ_{Mo}) (symbols as in Fig. 6)

The above concept was supported by the application of the non-isothermal kinetic equation (Eq. (4)) to evaluate the values of E_a and A for the studied catalysed thermal decomposition process. The obtained values (as seen in Fig. 8) lie in the sequence $BiP < Bi_2(HP)_3 < Bi(H_2P)_3 < H_3P <$ pure malonic acid, i.e. the same sequence as for the decrease in δ_{Mo}. This allows the inference that the activation energy decrease runs parallel to the accelerating effect of the different catalysts, which is proportional to δ_{Mo}.

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Zusammenfassung — Mittels Gasometertechnik bei atmosphärischem Druck wurde eine vergleichende Betrachtung der isothermen und nichtisothermen Zersetzung von Malonsäure durchgeführt. Die Ergebnisse zeigen unter isothermen Bedingungen zwei verschiedene Mechanismen. Während die Zersetzungsprozesse bei niedrigeren Temperaturen durch eine Reaktionskinetik erster Ordnung bestimmt werden, findet bei höheren Temperaturen die Randomkeimbildungsgleichung von Erofeev Anwendung. Diese Technik konnte bei der Auswertung der nichtisothermen TG-Kurven vorteilhaft angewendet werden. Sie liefert schnelle und stichhaltige Informationen über die thermische Zersetzungkinetik von Malonsäure sowohl rein als auch in Gegenwart eines Katalysators, der in Form von 12-Molybdatophosphorsäure oder deren Bismutsalzen als Feststoffkatalysator beigemischt wird. Auf der Basis der Anwendbarkeit der nichtisothermen Kinetikgleichung konnte gezeigt werden, daß der Verstärkungseffekt dieser Katalysatoren hauptsächlich auf Faktoren elektronischer Natur zurückgeführt werden kann.

Резюме — С помощью газометрии при атмосферном давлении проведено сравнительное изучение изотермического и неизотермического разложения малоновой кислоты. Результаты, полученные в изотермическом режиме, показали два различных механизма. При более низких температурах процесс разложения описывается кинетическим урвнением первого порядка, тогда как при более высоких температурах он контролируется произвольным образованием центров кристаллизации согласно уравнению Ерофеева. Анализ неизотермических кривых ТГ показал преимущество данного метода. Этот метод дает быструю и точную информацию о кинетике термического разложения малоновой кислоты, как чистой, так и в присутствии таких твердых катализаторов, как смесь 12-молибденофосфорной кислоты и ее висмутовых солей. Исходя из применимости неизотермического кинетического уравнения, было показано, что усиливающее влияние этих катализаторов носит электронный характер.