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Note

KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION OF SOME ACID TEREPHTHALIC ESTERS. A THERMOGRAVIMETRIC STUDY

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1-Phenylethyl hydrogen terephthalate (I), 1-(*p*-ethyl)-phenylethyl hydrogen terephthalate (II) and 1-(*p*-*tert*.-butyl)phenylethyl hydrogen terephthalate (III) have been subjected to thermogravimetric studies under non-isothermal and isothermal conditions. Mathematical analyses of the TG data have been made on the basis of mechanistic and mechanism non-invoking equations for obtaining the kinetic parameters. The Coats and Redfern equation [1] was used for general kinetic study. Various mechanistic model equations [2,3] have been employed for the mechanism-based analysis to obtain the probable operating mechanism. In the light of a recent illustration [4] for the need of carrying out a parallel isothermal run to have a better understanding of the mechanism, the TG data of the compounds obtained under isothermal conditions were also analysed using appropriate equations.

EXPERIMENTAL

The acid esters were prepared in very pure state by known methods [5]. The dried and powdered (mesh 200—240) materials were preserved in a desiccator before use. TG traces of 40 mg samples were recorded on a "Stanton" thermobalance (model TR-1). The heating rate was 4°C min^{-1}, for the non-isothermal runs. Independent pyrolytic studies under controlled conditions of temperature were made for isolating and characterising the products. The IR spectrum of the product of the first stage of II was recorded on a Perkin-Elmer IR spectrophotometer.

RESULTS AND DISCUSSION

The compounds gave well-defined and non-overlapping TG traces. The TG and DTG curves of II are given as illustration in Fig. 1. The weight loss during the first stage of the decomposition in each case was 16 ± 1, 17 ± 0.5, and 19 ± 0.5 mg for I, II and III, respectively, and these values agree with the removal of the corresponding styrene. Prior to decomposition the esters melted and rapid solidification occurred at the onset of the reaction. The IR

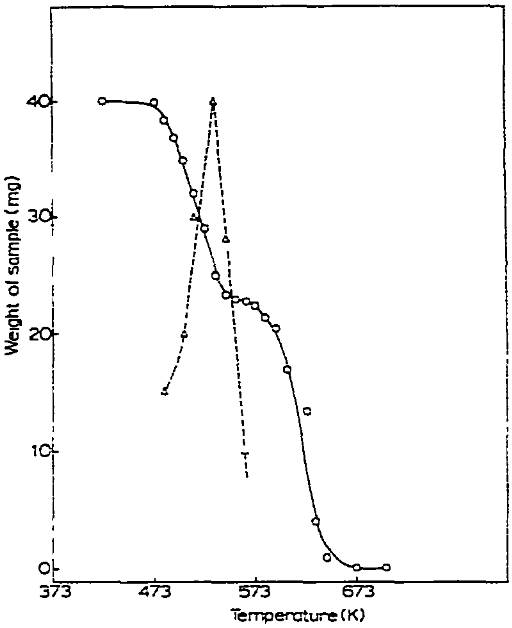


Fig 1 TG and DTG plots of 1-(p-ethyl)phenylethyl hydrogen terephthalate. ⊙, TG; ▲, DTG.

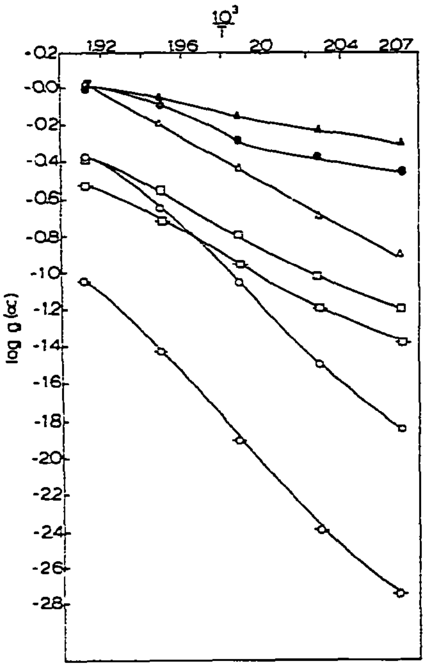
spectrum examined as thin film showed absorption characteristic of a p-disubstituted styrene (aromatic vinyl C—H stretching between 3000 and 3080, C=C vinyl stretching at 1620, C—H vinyl out-of-plane bending at 900 and 980) and a strong absorption characteristic of p-disubstituted benzene derivatives at 830 cm^{-1}. The residue remaining after the first stage was analysed and found to be 99.5% terephthalic acid. The temperature of initiation and temperature of completion of the second stage in all cases agreed with the TG trace of pure terephthalic acid. The first stage of the decomposition, being the more interesting, was selected for detailed kinetic study.

The mechanism-based model equations for f(α) [where f(α) is a function of the fractional decomposition, α] used for obtaining the g(α) functions were identical with those employed elsewhere [2,3]. Plots of g(α) vs. $1/T$ were made and from the linear plots, energy of activation, E^*, frequency factor, Z, etc. were calculated using known methods [6]. The f(α) function governing the rate-controlling process was found to be $(1-\alpha)$. Considering the fact that in the case of decompositions occurring over large ranges of temperatures, the g(α) values for even the most fitting mechanism need not necessarily vary linearly over the whole range. Zsako's [7] method of testing the validity of different kinetic equations based on mechanistic models and of determining the apparent activation energy consistent with a given set of g(α) functions was applied, and the δ values were found to be very small, in the range 0—0.002 for the mechanism found more probable for the decompositions. However, it may be noted that the temperature range for more than 99% decomposition in these cases is only around 483—533 K. The activation parameters and the probable operating mechanism are given in Table

TABLE 1

Activation parameters

Compound	Coats—Redfern equation			Mechanistic equation (Mampel model)	
	E^* (kJ mole^{-1})	Z (sec^{-1})	ΔS^* (deg^{-1})	E^* (kJ mole^{-1})	Z (sec^{-1})
1-phenylethyl hydrogen terephthalate	107.2	1.55×10^8	−92.9	102.9	6.03×10^7
1-(*p*-ethyl)phenylethyl hydrogen terephthalate	111.6	4.7×10^8	−83.6	106.2	1.32×10^8
1-(*p*-*tert.*-butyl)-phenylethyl hydrogen terephthalate	148.4	2.24×10^{12}	−13.4	144.8	9.33×10^{11}



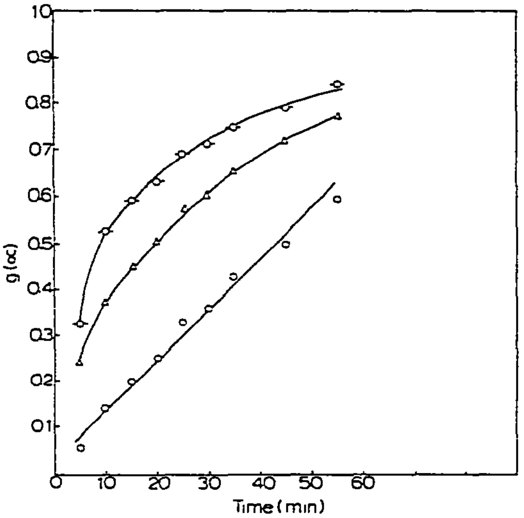


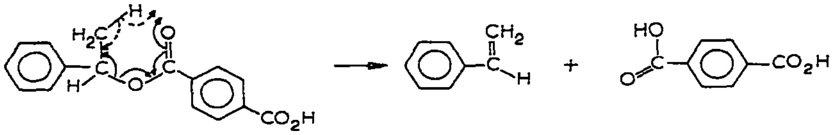
Fig 2. Plots of log g(α) vs $10^3/T$ for 1-(*p*-ethyl)phenylethyl hydrogen terephthalate. ⊙, $g(\alpha) = \alpha^2$; —⊙—, $g(\alpha) = [1 - (1 - \alpha)^{1/3}]^2$, △, $g(\alpha) = -\ln(1 - \alpha)$, ●, $g(\alpha) = [-\ln(1 - \alpha)]^{1/2}$; ▲, $g(\alpha) = [-\ln(1 - \alpha)]^{1/3}$, ⊡, $g(\alpha) = [1 - (1 - \alpha)]^{1/2}$; —⊡—, $g(\alpha) = [1 - (1 - \alpha)]^{1/3}$

Fig. 3. Plots of g(α) vs. time for 1-phenylethyl hydrogen terephthalate ⊙, $g(\alpha) = -\log(1 - \alpha)$, △, $g(\alpha) = [-\log(1 - \alpha)]^{1/2}$; —⊙—, $g(\alpha) = [-\log(1 - \alpha)]^{1/3}$.

1. The influence of the functions g(α) on $1/T$ is shown as an illustration for the decomposition of II in Fig. 2.

Criado and Morales [8], basing arguments on their theoretical analysis, stressed the need for recording an isothermal run of the same reaction at a temperature in the temperature range of decomposition of the non-isothermal run, for assigning the appropriate g(α) function unequivocally. Accordingly the data obtained from isothermal runs were analysed assuming the Avrami and Erofeyev [9,10] relation, viz. $g(\alpha) = [-\log(1 - \alpha)]^{1/n} = kt$, where n can be 1, 2 or 3 and k is rate constant. Illustrative plots of g(α) vs. time for the isothermal decomposition of I are given in Fig. 3. The first stage of decomposition of all the esters gave the value of n as unity. This agreed perfectly with the mechanism found probable from the non-isothermal method. The mechanism-based kinetic analysis of the non-isothermal TG data fitted best with $f(\alpha) = (1 - \alpha)$. Hence it turns out that the decomposition occurs according to the Mampel [11] equation, characterised by random nucleation.

The activation parameters, viz. the energy of activation and entropy of activation (Table 1), are in favour of a mechanistic pathway for the decomposition proceeding through the formation of a six-membered cyclic transition state. Being a thermal reaction, homolytic bond cleavage in the cyclic transition state is more likely than heterolysis, and the mechanism is comparable to that of the McLafferty rearrangement in the mass spectral fragmentarion of similarly constituted esters. The course of the reaction may, therefore, be depicted as



Cyclic transition states have been invoked [12] in the pyrolyses of low molecular weight carboxylic esters and polyethylene terephthalates.

Thus, pyrolysis of the acid terephthalic esters of 1-phenylethyl alcohol and its *p*-ethyl and p-*tert.*-butyl derivatives proceed via a cyclic transition state giving rise to styrenes and terephthalic acid in the first stage according to the rate law

$$\frac{d\alpha}{dt} = k(1 - \alpha)$$

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