Kinetic Parameters in Polypropylene Degradation From DTA Traces

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Synopsis

A novel and relatively simple procedure is described for the estimation of kinetic parameters in pyrolyses from DTA traces. The expressions derived are tested by utilizing data from experimental thermograms. Calculated values of parameters agree well with reported values.

INTRODUCTION

Various reports have appeared in the literature which describe non-isothermal methods for the estimation of overall activation energy E and reaction order n in polymer degradation by means of thermogravimetric (TGA) techniques.[1-5] In many of these methods, both E and n may be simultaneously or separately determined. Methods have also been reported for the estimation of kinetic parameters in thermal decomposition by means of DTA techniques. However, in these methods, E and n are evaluated by trial-and-error procedures,[6,7] or E is estimated after assuming a value of n,[8-10] or E is estimated after obtaining a value of n from TGA traces.[11] In order to overcome such shortcomings, a method was developed whereby both E and n may be obtained directly from DTA traces. This method was tested by applying it to the decomposition of simple inorganic and organic substances, and finally to polypropylene decomposition.

THEORY

In the estimation of kinetic parameters from TGA traces, it was recently reported[12] that the following expressions were applicable:

$$E/R = S/[W_c \ln (W_{0,c}/W_c)] \qquad n = 1 \qquad (1)$$

$$E/R = S(1 - n)/W_c^n(W_{0,c}^{(1-n)} - W_c^{(1-n)}) \quad n \neq 1 \qquad (2)$$

$$S_1/S_2 = (W_{1,c}/W_{2,c})[\log (W_{0,c}/W_{1,c})/\log (W_{0,c}/W_{2,c})] \qquad n = 1 \qquad (3)$$

and

$$S_1/S_2 = (W_{1,c}/W_{2,c})^n[1 - (W_{1,c}/W_{0,c})^{(1-n)}/1 - (W_{2,c}/W_{0,c})^{(1-n)}]$$
$$n \neq 1 \qquad (4)$$

where $W_c = W - W_r$; W = weight or weight fraction of material remaining, and W_r = weight or weight fraction of inactive material remaining after a pyrolysis;

$$S = dW_c/d(1/T)$$

and

$$W_{0,c} = W_0 - W_r$$

By assuming that heat capacity terms are negligible in comparison with other terms and that the cell constants for the sample and reference cells are about equal, it may be shown[6,13] that

$$-dW_c/dT \cong W_{0,c}(\Delta T/A_T) \tag{5}$$

and

$$W_c \cong W_{0,c}(\tilde{a}_T/A_T) \tag{6}$$

where

$$\tilde{a}_T = \int_{Ti}^{\infty} \Delta T dT - \int_{Ti}^{T} \Delta T dT$$

$$A_T = \int_{Ti}^{\infty} \Delta T dT$$

and ΔT is the height of the DTA curve.

By inserting eqs. (5) and (6) into eqs. (1)–(4), the following expressions may be obtained,

$$E/R = T^2 \Delta T/\tilde{a} \ln (A/\tilde{a}) \qquad n = 1 \tag{7}$$

$$E/R = [(1 - n)T^2 \Delta T/A_T]/(\tilde{a}_T/A_T)^n[1 - (\tilde{a}_T/A_T)^{(1-n)}] \qquad n \neq 1 \tag{8}$$

$$\left(\frac{T_1}{T_2}\right)^2 \left(\frac{\Delta T_1}{\Delta T_2}\right) \equiv F(T) = \left(\frac{\tilde{a}_{T,1}}{\tilde{a}_{T,2}}\right) \frac{\log (A_T/\tilde{a}_{T,1})}{\log (A_T/\tilde{a}_{T,2})} \qquad n = 1 \tag{9}$$

and

$$F(T) = (\tilde{a}_{T,1}/\tilde{a}_{T,2})^n \left[\frac{1 - (\tilde{a}_{T,1}/A_T)^{(1-n)}}{1 - (\tilde{a}_{T,2}/A_T)^{(1-n)}}\right] \qquad n \neq 1 \tag{10}$$

TESTING OF THE THEORETICAL EQUATIONS

In order to test the equations previously developed, DTA traces reported for inorganic and organic samples were utilized. Thus, DTA traces for an aqueous solution of benzenediazonium chloride,[6,7] sodium bicarbonate,[14] calcium oxalate monohydrate,[15] and bulk polypropylene[16] were employed. The first case represents an almost ideal situation in which cell constants, heat capacities, and volume terms are almost identical for the sample and reference cells. In order to minimize differences in these values when solids are pyrolyzed, a sample packing technique is often
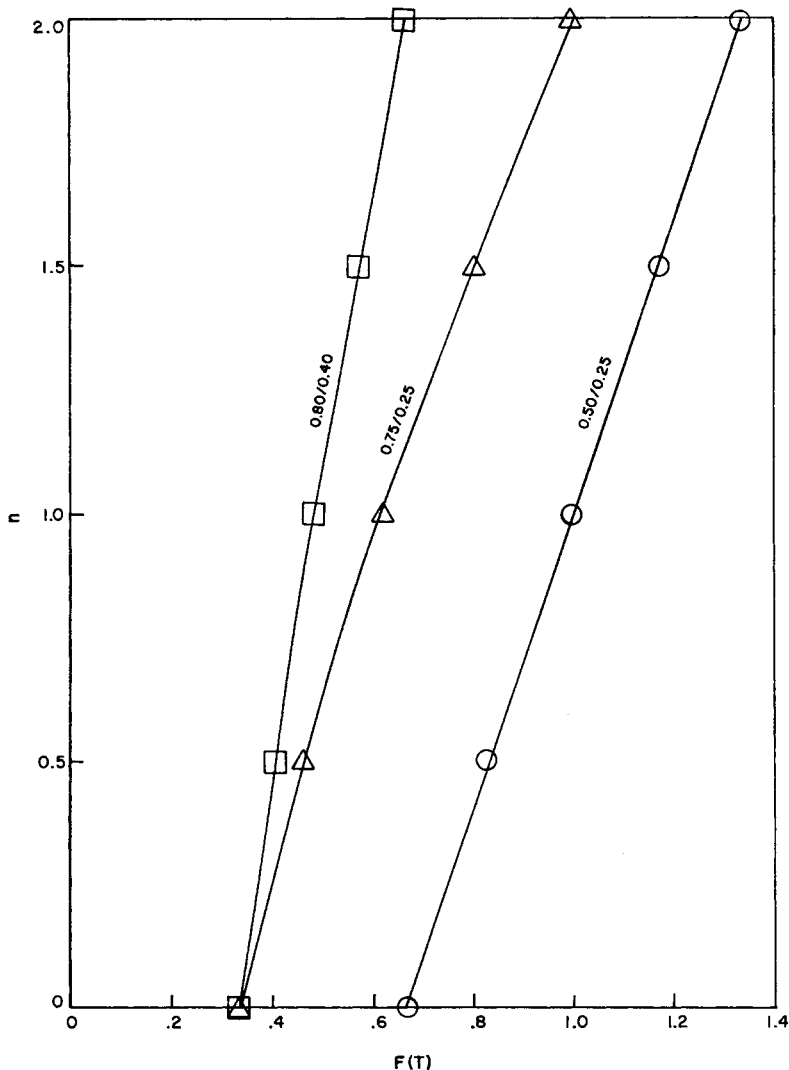
Fig. 1. Reaction order n as a function of $F(T)$ for various values of the ratio $(\bar{a}_{T,1}/A_T)/(\bar{a}_{T,2}/A_T)$.

employed which involves the dilution of the samples with the reference material (usually alumina) being used. As a result of such an admixture, packing and thermal properties will be determined mainly by the reference material, regardless of sample shrinkage, melting, decomposition, etc. The polypropylene studied involved such a packing[16] and the purging of the sample with nitrogen involved a gas diffusion (GD) and a dynamic gas flow process (DGF). However, in the cases of sodium bicarbonate and calcium oxalate monohydrate, no admixture of the sample with reference material was made.

In determining kinetic parameters in thermal decompositions by DTA techniques, it must be ascertained that over the apparent decomposition peak no other changes are occurring which are endothermic, exothermic, or which involve changes in mechanism. It may also be noted that overall kinetic parameters, obtained by the expressions previously mentioned, cover the entire sample conversion range.

Estimation of n

Prior to determining the overall activation energy of a pyrolysis by the procedures employed in this paper, it is necessary to estimate the reaction order, n. From eqs. (9) and (10), it can be seen that $F(T)$ may be plotted as a function of n for various values of $(\tilde{a}_{T,1}/A_T)$ and $(\tilde{a}_{T,2}/A_T)$. In Figure 1 is shown such a plot with values of the latter ratios listed alongside each curve. Values of the sample temperature T and the height of the thermogram ΔT were obtained, where $(\tilde{a}_T/A_T)$ possessed the desired value on the thermogram. In obtaining values of areas, a compensating polar planimeter was employed. After a few rapid trial-and-error tracings of the thermogram with the planimeter, the sample temperature and peak height corresponding to the ratio $(\tilde{a}_T/A_T)$ could be readily obtained. From the values of ΔT and T, $F(T)$ could be calculated and the curves in Figure 1 were then utilized to estimate values of n for various DTA thermograms. These values are listed in Table I and are in satisfactory agreement with reported values. In this connection, it may be mentioned that in the case of polypropylene, when a DGF purge was employed, the value of n dropped from an average value of 0.89 for the GD process to an average value of about 0.7; however, for both processes, the value of E was about the same. Thus, the manner in which the sample is purged does not appear appreciably to affect values of kinetic parameters during polypropylene pyrolysis.

Estimation of E

After the value of n has been estimated as described above, a value of E may be calculated for each ratio, $(\tilde{a}_T/A_T)$, by means of eq. (7) or (8). In Table I are listed average values of E for the various materials studied. These values represent the averages of the two ratios listed in column 3 of Table I and are in good agreement with reported values of E. After values of E and n have been estimated, the value of the frequency factor, Z, may be ascertained subsequently, as described below.

Estimation of Z

If, as has been assumed, the Arrhenius equation is valid in pyrolyses, one may write,

$$R_T = [Z/(RH)] \exp\{-E/RT\} W_c^n \qquad (11)$$

TABLE I

Values of E, n, and Z for Various Materials by Eqs. (7)–(10), (12)

Material or reaction	(RH), °C./min.	$\left[\dfrac{(\bar{a}_{T,1}/A_T)}{(\bar{a}_{T,2}/A_T)}\right]$	Reaction order n		Activation energy E, kcal./mole		Frequency factor Z, min.$^{-1}$	
			Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
Aq. soln. of benzenediazonium chloride	1	0.50/0.25 0.75/0.25 0.80/0.40	1.0 1.0 1.1	1.0[a,b,c]	28 ± 0.5 28 ± 0.9 28 ± 0.8	28.3[a] 28.7[c]	$(1.2 \pm 0.1) \times 10^{18}$	$1.3 \times 10^{18[a]}$ $2.5 \times 10^{18[c]}$
NaHCO$_3$ (in still air)	3$^{1}/_{2}$	0.50/0.25 0.75/0.25 0.80/0.40	0.77 0.68 0.78	0.79–0.83[d]	23 ± 0.5 22 ± 0.5 22 ± 0.5	22–25[d]		
CaC$_2$O$_4$·H$_2$O → CaC$_2$O$_4$ + H$_2$O (in air)	8	0.50/0.25	0.98	1.0[e]	22 ± 0.5	22[e]		
CaC$_2$O$_4$ → CaCO$_3$ + CO (in air)	8	0.50/0.25	1.0	0.7[e]	70 ± 1	74[e]		
CaCO$_3$ → CaO + CO$_2$ (in air)	8	0.50/0.25	0.40	0.4[e]	48	39[e]		
Polypropylene (GD) (in nitrogen)	10	0.50/0.25 0.75/0.25 0.80/0.40	0.88 0.78 1.0	1 (over a limited conversion range)[f]	58 56 61	58[f] 55[g] 62.5[h] 65[i]	$(5.9 \pm 0.1) \times 10^{17}$	$2.2 \times 10^{17[j]}$

[a] Data of Borchardt and Daniels.[6]

[b] Data of Borchardt.[7]

[c] Data of Reed et al.[13]

[d] Data of Reich.[14]

[e] Data of Freeman and Carroll.[5]

[f] Data of Madorsky.[17]

[g] Data of Moiseev et al.[18]

[h] Data of Bresler et al.[19]

[i] Data of Davies et al.[20]

[j] Estimated from data of Madorsky[17] at 366°C.

where

$$R_T = -dW_c/dT$$

and (RH) denotes the rate of heating, which is constant.   By inserting eqs. (5) and (6) into eq. (11), there is obtained,

$$\log Z = (E/2.3RT) + \log [\Delta T(RH)/A_T]$$

$$+ n \log (A_T/\tilde{a}_T) - (n - 1) \log W_{0,c} \quad (12)$$

If Z is to be expressed in terms of reciprocal time, then $W_{o,c}$ must be expressed in terms of weight fraction (except for $n = 1$).   Thus, the last term in eq. (12) may in many instances be neglected in comparison with the other terms.   By utilizing this simplification of eq. (12), average values of Z, in reciprocal minutes, were obtained for two ratios of $(\tilde{a}_T/A_T)$ in the cases of benzenediazonium chloride and polypropylene.   The reported values were found to agree well with the calculated values of Z.
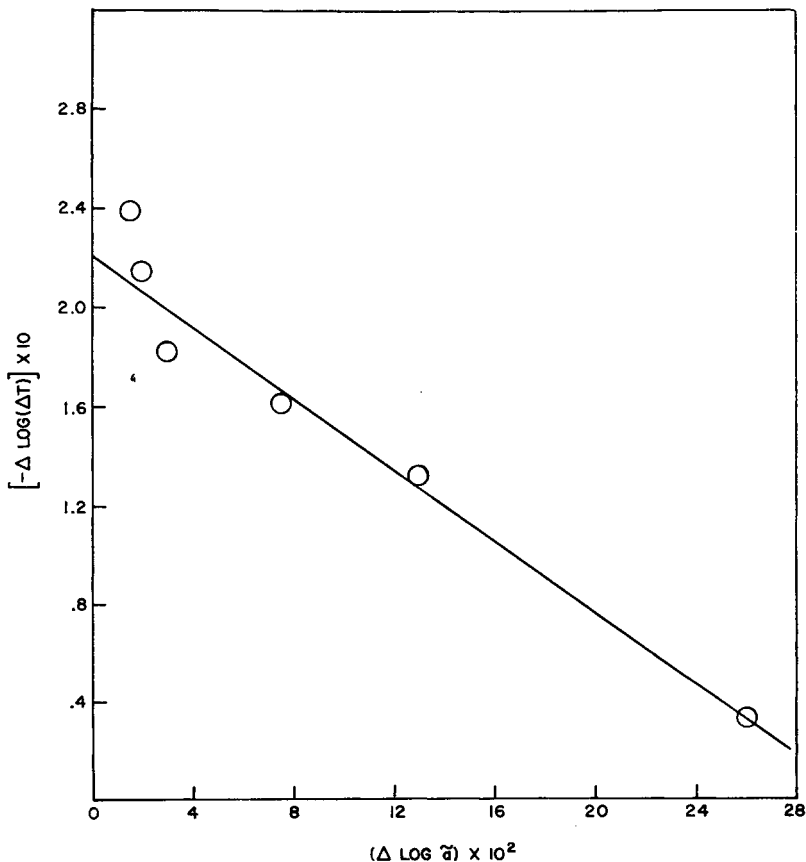

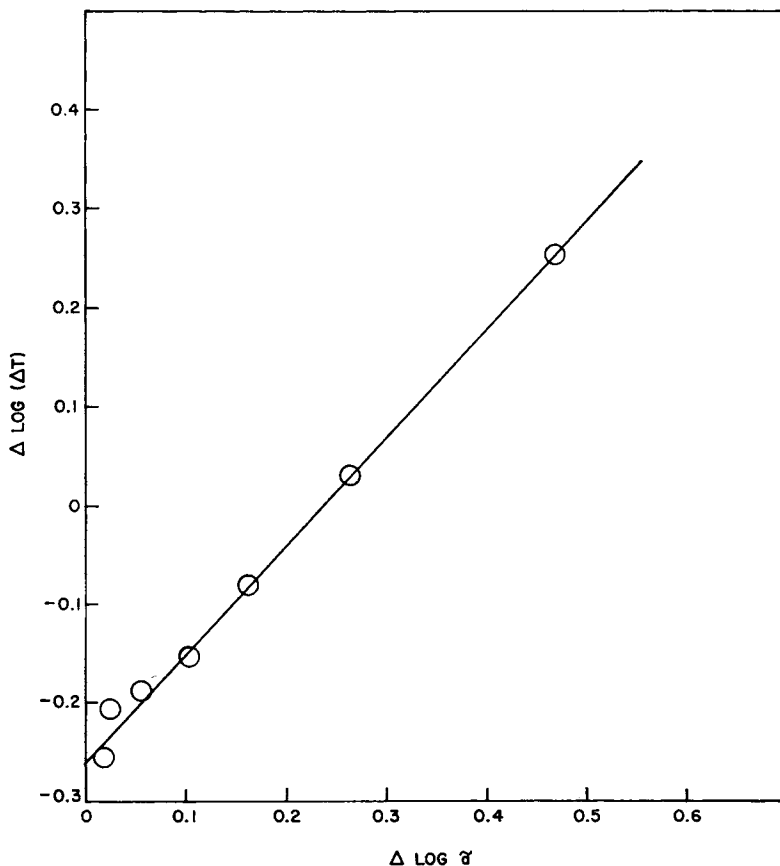Fig. 2. $\Delta \log (\Delta T)$ vs. $\Delta \log \tilde{a}$ for polypropylene (GD).

Fig. 3. $\Delta \log (\Delta T)$ vs. $\Delta \log \tilde{a}$ for benzenediazonium chloride.

OTHER TECHNIQUES

It seems appropriate in this paper to mention and apply another technique for the estimation of E and n from DTA traces.   This method has been previously reported[5] but has not been applied, to the best of our knowledge. The method is sensitive to error, and, unless great care is exercised, the appropriate plot for estimating E and n may contain points with consider-able scatter.   By making the same assumptions, as previously mentioned in respect to heat capacity and cell-constant terms, the following expression may be readily obtained [cf. eq. (17) in ref. 5],

$$\Delta \log (\Delta T) = n\Delta \log \tilde{a} - (E/2.3R)\Delta(1/T) \tag{13}$$

From eq. (13), it can be seen that when $\Delta(1/T)$ is held constant, then a plot of $\Delta \log (\Delta T)$ versus $\Delta \log \tilde{a}$ should give a linear relationship whose slope will afford the value of n and whose intercept the value of E.   In Figures 2 and 3 are shown such plots for polypropylene and benzenediazonium chloride, respectively.   The following values of E and n were obtained for

polypropylene and benzenediazonium chloride, respectively, 54, 0.73; 30, 1.1. These values are in good agreement with those listed in Table I for the above materials.

It is hoped to apply the above methods to various other polymers.

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Résumé

Un procédé nouveau et relativement simple est décrit pour permettre l'estimation de paramètres cinétiques au cours des pyrolyses au départ d'indications provenant de l'analyse thermique différentielle. Les expressions dérivées ont été testées en utilisant lez données provenant de thermogrammes expérimentaux. Les valeurs calculées de paramètres s'accordent bien avec les valeurs rapportées.

Zusammenfassung

Ein neues und verhältnismässig einfaches Verfahren zur Bestimmung kinetischer Pyrolyseparameter aus DTA-Kurven wird beschrieben. Die abgeleiteten Ausdrücke werden an Daten aus experimentellen Thermogrammen überprüft. Die berechneten Werte der Parameter stimmen gut mit bekannten Werten überein.