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THE KINETICS OF POLYMER DECOMPOSITION THROUGH THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT

This study introduces a new method (the ratio method) of analyzing thermograms for which the power-model kinetic equation is assumed to hold. This method can be used to determine the kinetic parameters from a single thermogram obtained by decomposing a material at a constant heating rate. In this paper, the ratio method, the maximum-point method, and the method of Freeman and Carroll are compared regarding their respective accuracy and ease of interpreting the kinetics of thermal decomposition.

NOMENCLATURE

b = heating rate
i, j = subscripts indicating position on the thermogram
n = reaction order
t = time
E = activation energy
K = frequency factor
R = gas constant
T = absolute temperature
T_0 = initial temperature
W = weight at any time t
W_f = final weight
W_0 = initial weight
γ = fraction remaining, $\dfrac{W-W_f}{W_0-W_f}$

γ_m = the fraction remaining at the maximum rate of weight loss
T_m = the absolute temperature at the maximum rate of weight loss
$\left(-\dfrac{d\gamma}{dT}\right)_m$ = maximum rate of weight loss

INTRODUCTION

Although there are many methods for analyzing thermogravimetric data in order to determine the kinetic constants that govern thermal decomposition, the two most popular seem to be the maximum-point method[1,2,4] and the method of Freeman and Carroll[3]. Both methods have the advantage that only one thermogram obtained by heating the sample at a constant rate needs to be used for determining all of the kinetic constants.

The maximum-point method has the advantage that many thermograms can be analyzed in a short period of time. However, since only one point (the point where the rate of decomposition is a maximum) is used, there is no way to know whether the power-model kinetic equation is valid over the entire decomposition range.

The method of Freeman and Carroll does use a major portion of the thermogram for determining the kinetic constants. Therefore, if there are any changes in the decomposition mechanism, these changes will be evident by the non-linearity on a graphical plot of the data. The major disadvantage of this method is that it requires the determination of a number of slopes accurately if a good kinetic analysis is to be made. Because of the involved analytical procedure necessitated by this method, the time involved in analyzing thermograms becomes excessive.

A new method (termed the "ratio method") of analyzing thermograms for which the power-model kinetic equation is assumed to hold is introduced in this study. This method has the same advantage as the Freeman and Carroll method in that a major portion of the thermogram is used to determine the kinetic constants. However, for the ratio method, only one slope, that of the decomposition rate, needs to be determined accurately. This method is ideally suited for those thermoanalyzers that provide differential thermogravimetric analysis (DTG). In addition, this method is readily adaptable for use with computers in the analysis of thermograms.

In order to illustrate the use of the ratio method, samples of a urethane polymer were decomposed at two different heating rates and analyses of the thermograms were made. The kinetic parameters obtained using the ratio method were compared to those recorded when the thermograms were analyzed using the maximum-point and the Freeman–Carroll methods.

THEORY

Kinetic analyses at constant heating rates

A simple model equation in the form:

$$(-\mathrm{d}\gamma/\mathrm{d}t) = K\exp(-E/RT)\gamma^n \tag{1}$$

is often chosen as representing the kinetics for polymer decomposition. For a constant heating rate, the temperature can be expressed as a linear function of time:

$$T = T_0 + bt \tag{2}$$

where

T_0 = initial temperature
b = heating rate

Now, Eqn. (2) can be used to eliminate time as a variable from Eqn. (1):

$$(-\mathrm{d}\gamma/\mathrm{d}T) = \frac{K}{b}\exp(-E/RT)\gamma^n \tag{3}$$

This is the form used in the treatment of data by either the method of Freeman and Carroll, or the maximum-point method.

The Freeman and Carroll method

This is one of the first and the most popular method of treating thermogravimetric data. By taking the logarithm of both sides of Eqn. (3) and then differentiating with respect to temperature, they obtained Eqn. (4).

$$\frac{\mathrm{d}\log(-\mathrm{d}\gamma/\mathrm{d}T)}{\mathrm{d}\log\gamma} = n + \frac{E}{2.303\,R}\cdot\frac{\mathrm{d}T}{T^2\,\mathrm{d}\log\gamma} \tag{4}$$

Eqn. (4) predicts that a straight-line relationship exists when $\mathrm{d}\log(-\mathrm{d}\gamma/\mathrm{d}T)/\mathrm{d}\log\gamma$ is plotted *vs.* $\mathrm{d}T/(T^2\,\mathrm{d}\log\gamma)$. The intercept determines n and the slope is equal to $E/2.303\,R$. The frequency factor, K, is determined by using Eqn. (3). Thus, from a single thermogram, the kinetic parameters can be determined.

As mentioned earlier, the main difficulty in using this equation is the necessity of determining several slopes accurately. Not only must the slope $(-\mathrm{d}\gamma/\mathrm{d}T)$ be determined precisely, but also the slopes $\mathrm{d}\log(-\mathrm{d}\gamma/\mathrm{d}T)$ and $\mathrm{d}\log\gamma$. Moreover, since $\mathrm{d}\log\gamma$ appears in the denominator of both variables, any errors occurring either while collecting the data or during the treatment of the data may go unnoticed.

The maximum-point method

Because thermograms of polymer decomposition show that the rate of decomposition has a maximum value, the kinetic parameters can be determined upon locating the point where this maximum occurs. The following relationships are used to determine the kinetic parameters.

$$n = \gamma_m^{1/n} \qquad \text{for } n \neq 1 \tag{5}$$

$$n = 1 \qquad \text{when } \gamma_m = 1/e \tag{6}$$

$$E = \frac{nRT_m^2}{\gamma_m}\left(-\frac{\mathrm{d}\gamma}{\mathrm{d}T}\right)_m \tag{7}$$

$$K = \frac{bE}{RT_m^2}\exp\left(\frac{E}{RT_m}\right) \tag{8}$$

The calculations involved in determining the kinetic parameters are simple to perform, thereby permitting the researcher to examine many thermograms in a short time. However, the kinetic parameters are determined from a single point on the thermogram, which is a major disadvantage. This means that the researcher must blindly accept the power-model equation as representing the kinetics for the decomposition of his polymer. Flynn and Wall[2] discuss the uniqueness of thermograms and demonstrate how difficult it would be to determine reliable activation energies using the maximum-point method.

The ratio method

Because of the inherent difficulties that are found in the methods described above, these authors have formulated another method for treating the data obtained from a single thermogram where the polymer has been decomposed at a constant heating rate. From Eqn. (1) it is seen that $(-\mathrm{d}\gamma/\mathrm{d}t)$ and γ, can be determined at any temperature T, so that,

$$(\mathrm{d}\gamma/\mathrm{d}t)_i = K \exp(-E/RT_i)\gamma_i^n \tag{9}$$

At any other temperature, the values of $(-\mathrm{d}\gamma/\mathrm{d}t)$ and γ can also be determined. Using the subscript j to denote this case, the following equation applies:

$$(-\mathrm{d}\gamma/\mathrm{d}t)_j = K \exp(-E/RT_j)\gamma_j^n \tag{10}$$

By taking the ratio of Eqn. (9) to Eqn. (10), the frequency factor can be eliminated:

$$(-\mathrm{d}\gamma/\mathrm{d}t)_i/(-\mathrm{d}\gamma/\mathrm{d}t)_j = \exp\{-E/R[(T_j-T_i)/T_iT_j]\}(\gamma_i\gamma_j)^n \tag{11}$$

Eqn. (12) results when logarithms of both sides of Eqn. (11) are taken:

$$\log[(-\mathrm{d}\gamma/\mathrm{d}t)_j/(-\mathrm{d}\gamma/\mathrm{d}t)_i] = (E/2.303\,R)[(T_j-T_i)/T_iT_j] - n\log(\gamma_i/\gamma_j) \tag{12}$$

The variables $\log(-\mathrm{d}\gamma/\mathrm{d}t)_j/(-\mathrm{d}\gamma/\mathrm{d}t)_i$ and $(T_j-T_i)/T_iT_j$ will plot as a straight line providing the ratio γ_i/γ_j is maintained constant. For example, if the ratio is set at 2, then,

$$\gamma_i/\gamma_j = 0.90/0.45 = 0.80/0.40 = 0.70/0.35\ldots$$

fulfills this condition and the slopes and temperatures are evaluated at each of these points. The activation energy can be determined from the slope of the line and the reaction order can be determined from the intercept.

Although the accuracy of this method does depend on determining the slope $(-\mathrm{d}\gamma/\mathrm{d}t)$ accurately, it does not require the determination of two more slopes as is necessitated by the method of Freeman and Carroll. The calculations are simple, and most important, the entire thermogram can be used in analyzing the kinetics of the reaction. Also, it is possible to analyze any portion of the thermogram by changing the ratio, γ_i/γ_j. The selection of the ratio dictates how many points will be obtained from a particular section of the thermogram. Ratios selected near unity require a very accurate knowledge of the temperature and the slope of the thermogram if any straight line is to be expected. This provides a check on the accuracy with which the data have been obtained.

Eqn. (12) can be represented in a slightly different from which helps in analyzing those thermograms where the weight of the sample is measured as a function of time as is the case for the Mettler Thermobalance. Because

$$\mathrm{d}\gamma/\mathrm{d}t = \mathrm{d}\{(W-W_f)/(W_0-W_f)\}/\mathrm{d}t = (1/W_0-W_f)(\mathrm{d}W/\mathrm{d}t) \tag{13}$$

then

$$(-\mathrm{d}\gamma/\mathrm{d}t)_j/(-\mathrm{d}\gamma/\mathrm{d}t)_i = (\mathrm{d}W/\mathrm{d}t)_j/(-\mathrm{d}W/\mathrm{d}t)_i \tag{14}$$

Also

$$\gamma_i/\gamma_j = (W_i-W_f)/(W_j-W_f) \tag{15}$$

These two considerations permit the direct use of the TGA curve without first transforming to the dimensionless term γ.

EXPERIMENTAL

A urethane polymer was prepared by reacting pure 2–4 toluene di-isocyanate with a polyol that had a molecular weight of 312 grams per gram mole and a functionality of three. No catalyst was used in the reaction. The polymer was cast into small slabs and cured at temperatures below 80 °C to insure that any biuret or allophonate formed as a side reaction would be minimal.

Special consideration must be given to the preparation of samples for the TGA. The gases evolved during decomposition must readily diffuse through the sample and be removed by the carrier gas. In order to determine the best method of preparing material for thermogravimetric analysis, a preliminary experiment was run in which samples of an 80:20 toluene diisocyanate–polyol urethane was cast into two thin sheets of different thicknesses. Samples from these two castings were cut so that they had the same weight, but different surface areas. These samples were run in a Dupont TGA isothermally at 243 °C. The results of this experiment are shown in Fig. 1. As can be seen, there is a decided difference in the rates at which the samples lose weight.

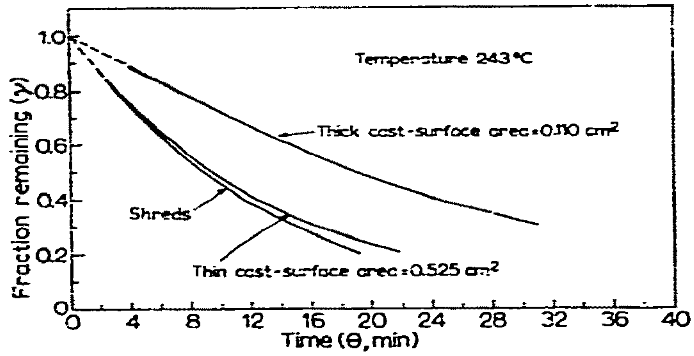

Fig. 1. The effect of sample condition on the isothermal decomposition of 80:20 TDI-urethane (Dupont TGA).

Another sample was prepared for TGA by shredding the polymer with a hacksaw. These shreds were about 150 microns thick by one millimeter or more in length. The polymer did not seem to suffer from heat or from mechanical decomposition as a result of the process of being shredded. This material was fluffy which prevented any packing on the weigh pan. These shreds were decomposed isothermally at 243 °C and as shown in Fig. 1, they decompose at a rate very similar to the thin cast polymer sample.

Another method of preparing samples was to file the solid polymer and collect the dust. This method produced sample material that was much smaller, varying from less than 10 microns to 200 microns in diameter. Both a shredded sample, weighing 6.86 mg, and a sample obtained by filing, weighing 6.80 mg, were decomposed isothermally at 269 °C in a Mettler Thermobalance. The results of this experiment are shown in Fig. 2. The sample made up of filings decomposed at a much slower rate than did the shredded sample. This slower rate indicates that the fine particles are packing on the pan and the diffusion of the evolved gases has become an important factor.

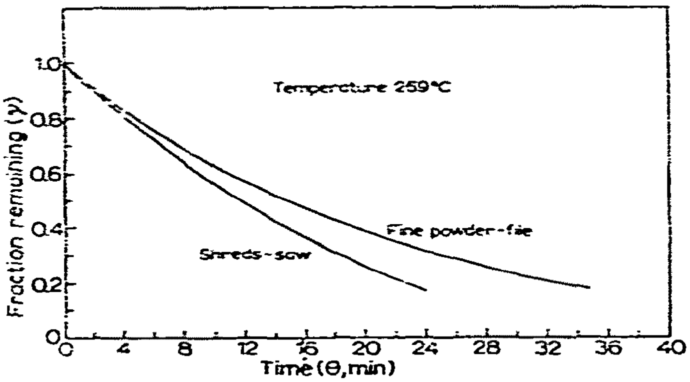

Fig. 2. The effect of sample condition on the isothermal decomposition of 2–4 TDI urethane.

Because the hacksaw method of shredding the sample produced thermograms that more closely matched the thermogram of the thin cast polymer material, and no other method was found to give as good a correlation, the hacksaw method was chosen for preparing all of the samples for thermogravimetric analysis.

For all of the kinetic work reported in this paper, a Mettler Thermoanalyzer was used.

DISCUSSION AND RESULTS

Shredded samples of urethane were run in the thermobalance at heating rates of 4 °C/min and 10 °C/min. Three samples were run at 10°/min. For two of these samples and also for the sample run at 4°/min, the initial weight was 6.8 mg. For the third sample, the initial weight was reduced to 4 mg to determine if the amount of material on the pan would affect the results. All of the samples were run in an argon atmosphere.

A typical thermogram for the decomposition of the materials is shown in Fig. 3. Both the amount of material remaining in the pan and rate at which the sample loses

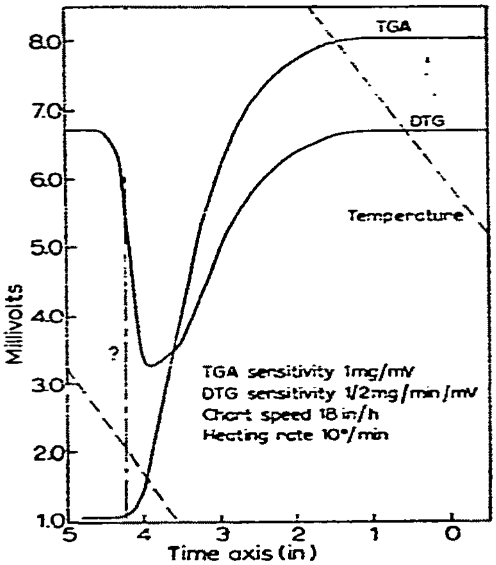

Fig. 3. Thermal decomposition of 2-4 TDI urethane (Mettler balance).

weight (DTG) are measured by the instrument. Along with these data, the sample temperature at the bottom of the pan is also measured. One aspect of the DTG data is that they lag behind the TGA curve in the final stages of decomposition since the DTG curve does not indicate a zero reaction rate after the TGA curve shows that there is no material left. A careful analysis of the TGA and DTG curves showed that this lag occurred only near the very end of each run. The recorded data can be transcribed into the more common form of fraction remaining *vs.* temperature as shown in Fig. 4.

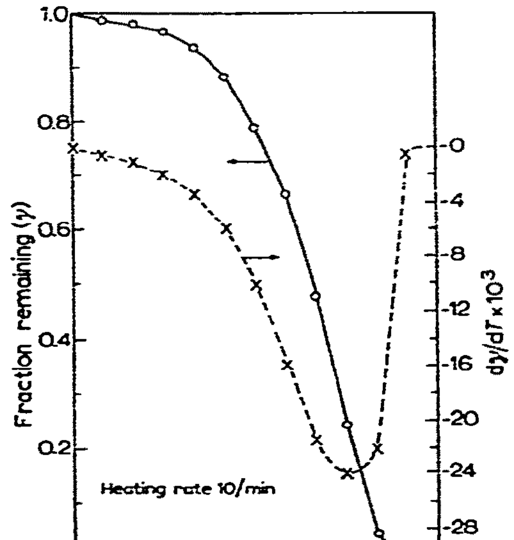

Fig. 4. Thermal decomposition of 2-4 TDI urethane as a function of temperature (Mettler balance).

The maximum-point method

The maximum-point method for determining the kinetic parameters was applied to the data and the results are presented in Table I.

TABLE I

DETERMINATION OF KINETIC PARAMETERS (MAXIMUM-POINT METHOD)

Heating rate (°/min)	*Activation energy (cal/gmole)*	*Reaction order*	*Frequency factor (min^{-1})*
4	37,600	0.46	6.3×10^{13}
10	36,000	0.59	26×10^{13}
10	31,000	0.47	1.6×10^{11}
10[a]	27,000	0.38	5.6×10^{9}

[a] Sample weight 4.0 mg.

These results indicate that this method gives widely varying answers. Of particular interest are the activation energies resulting from data obtained at a heating rate of 10°/min. These results show a variation of 9,000 cal/gmole in the activation energy for the decomposition of the polymer. Such a large variation supports the premise of Flynn and Wall about the difficulty in determining reliable activation energies using this method.

The Freeman and Carroll method

This method was also used to analyze the data and a summary of the results of this analysis are shown in Table II.

TABLE II

DETERMINATION OF KINETIC PARAMETERS (FREEMAN–CARROLL)

Heating rate (°/min)	*Activation energy (cal/gmole)*	*Reaction order*	*Frequency factor (min^{-1})*
4	34,600	0.50	4.58×10^{12}
10	33,400	0.70	2.18×10^{12}
10	30,300	0.50	1.29×10^{11}
10[a]	32,700	0.45	1.23×10^{12}

[a] Sample weight is 4.0 mg.

Here, it is shown that much better agreement is obtained between the activation energies calculated for heating rates of 10°/min. The variation in the activation energies from the highest value and the lowest value amounts to only ten percent. Also, the results obtained at a heating rate of 10°/min are in much better agreement with the result obtained at a heating rate of 4°/min.

The ratio method

The results of this method are presented in Table III.

TABLE III

DETERMINATION OF KINETIC PARAMETERS (RATIO METHOD)

Heating rate (*°/min*)	*Activation energy* (*cal/gmole*)	*Reaction order*	*Frequency factor* (*min*$^{-1}$)
4	33,200	0.46	1.32×10^{12}
10	33,200	0.55	1.51×10^{12}
10	30,500	0.61	1.55×10^{11}
10[a]	33,200	0.49	1.91×10^{12}

[a] Sample weight is 4.0 mg.

Except for the one run at 10°/min, there is excellent agreement between the activation energies obtained at heating rates of 4°/min and at heating rates of 10°/min.

The data presented in Fig. 5 represents a ratio of γ_i/γ_j of 1.5 to 1 and Fig. 6 represents a ratio of γ_i/γ_j of 3 to 1. By using high ratios such as 3 to 1, errors in measuring the temperature or the decomposition rate will produce less scatter in the data. Lower ratios such as 1.5 to 1 are more sensitive to these errors. For example, if the difference between temperatures T_j and T_i is large, then any error in measuring these temperatures will produce less scattering in the data. Lower ratios are more sensitive to the same errors because the difference between T_j and T_i gets smaller as the ratio gets smaller. However, as can be seen in Fig. 5, very little scatter exists indicating a reasonable accuracy in measuring those variables from which the kinetic parameters are determined.

For both the Freeman and Carroll method and the ratio method of analyzing kinetic data, only the portion of the thermogram from 90% undecomposed material

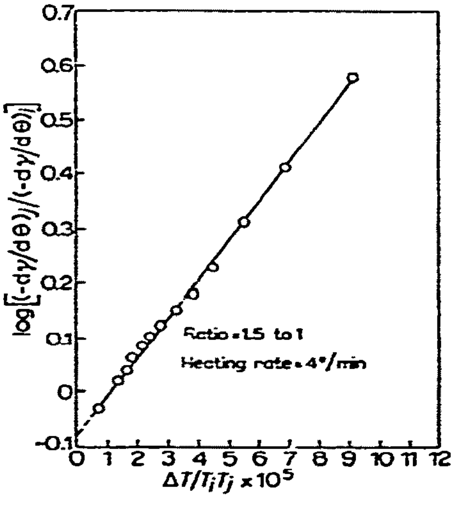

Fig. 5. The ratio method applied to decomposition at a low heating rate.

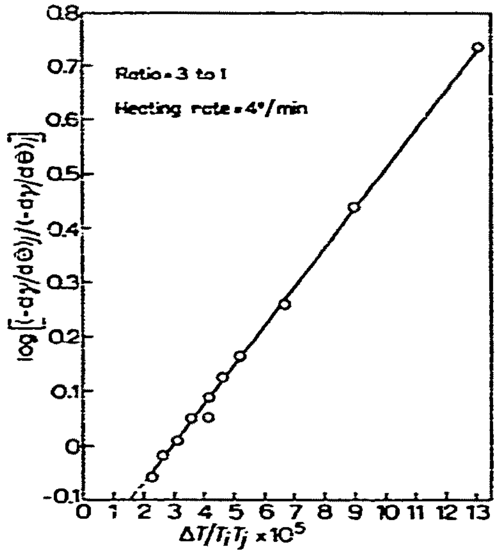

Fig. 6. The ratio method applied to decomposition at a low heating rate.

down to 10% undecomposed material was examined. This was done because either inaccuracies appear in measuring the thermal decomposition at the extremities of the thermogram or the power-model kinetic equation does not apply over the entire decomposition range. With the ratio method, it is possible to investigate the extremities of the thermogram and determine what deviations are occurring. If Eqn. (12) is rearranged into the following form:

$$\log\{(-\mathrm{d}\gamma/\mathrm{d}t)_j/(-\mathrm{d}\gamma/\mathrm{d}t)_i\}/\log(\gamma_i/\gamma_j) = \{E/2.303\,R\log(\gamma_i/\gamma_j)\}\{(T_j-T_i)/T_i T_j\} \tag{16}$$

a straight line should be obtained regardless of what ratio is used. It is permissible to divide by the $\log(\gamma_i/\gamma_j)$ because this quantity is a known constant and not a variable as is the case when dividing by $\mathrm{d}\log\gamma$.

An end point analysis is made for one of the samples heated at a rate of 10°/min and the results are shown in Fig. 7. The circles points cover a decomposition range from 90% undecomposed material down to 10% undecomposed material. The ratio γ_i/γ_j was varied from 9 to 1 down to 1.5 to 1. When the point corresponding to 95% of the material undecomposed is compared to other values of γ, the line represented by the designation, x, is obtained. This line shows that the earlier stages of decomposition definitely do not obey the same mechanism of decomposition as do the later stages. When the point corresponding to only 5% of the material remaining undecomposed is compared to other values of γ, a line indicated by the crosses is found to lie parallel to the original line. This indicates that the same activation energy governs the decomposition in the lower region, but the reaction order is slightly changed. The excellent fit of the data to the power-model kinetic equation over the major portion of the decomposition reaction indicates that this model equation is well-suited for explaining the decomposition kinetics of a simple urethane polymer.

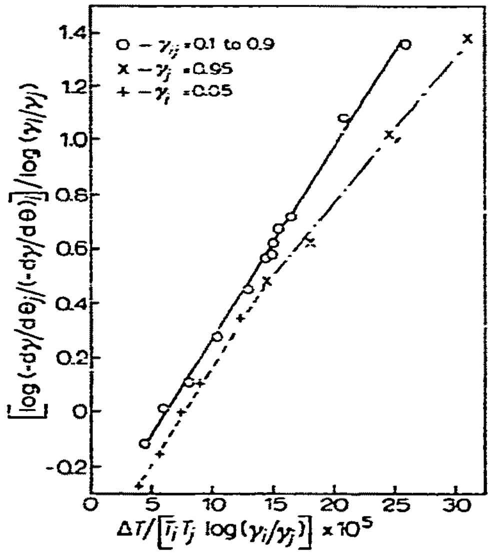

Fig. 7. End-point analysis of a thermogram.

CONCLUSIONS

The ratio method has proved to be a simple and accurate tool for determining kinetic constants. Just as in the method of Freeman and Carroll, the entire thermogram can be used in determining the kinetic parameters. However, in the ratio method, it is not necessary to determine the slopes of the logarithm of γ and of the logarithm of $(-d\gamma/dT)$ as is required by the method of Freeman and Carroll. Although the maximum-point method permits the rapid analysis of a thermogram, it has proved to be far less accurate than the ratio method or the method of Freeman and Carroll. Even though the ratio method is not as fast as the maximum-point method for examining thermograms, it is far more accurate and it is readily adaptable to the use of computers in the analyses of thermograms.

The entire thermogram should always be analyzed when determining kinetic parameters to insure that there is either no change in the reaction mechanism or that no competing reactions are occurring. If it is suspected that the decomposition reaction is not a simple one, then, separate portions of the thermogram can be examined by selecting ratios of γ_i/γ_j that give enough points to determine a reliable correlation covering the desired portion of the thermogram.

Although the main purpose of this investigation was to establish the validity to the ratio method for analyzing thermogravimetric data, it was found that for the urethane studied the kinetic equation is

$$(-d\gamma/dt) = 1.58 \times 10^{12} [\exp(-33{,}200/RT)] \gamma^{1/2} \text{ min}^{-1}$$

The one result at 10°/min where the activation energy is low is not included in determining the average value of the kinetic constants.

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