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THERMAL ANALYSIS OF REACTIONS AND TRANSFORMATIONS IN THE SOLID STATE. III. KINETIC STUDIES OF DESOLVATION, CHEMICAL DEGRADATION AND PHASE TRANSFORMATION USING THERMOGRAVIMETRY*

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ABSTRACT

The experimental applications of the previously introduced theoretical models were used to calculate the kinetic parameters of desolvation, chemical degradation, and phase transformation of five compounds of different chemical structures. These compounds are calcium oxalate monohydrate, anhydrous theophylline, urea, 50% filled ethylene/propylene rubber and unfilled cross-linked polyethylene. The approach produces kinetic parameters which are consistent, reproducible and independent of the experimental conditions. In addition, the new method allows the study of complex and overlapping reactions in both urea and polymer degradations. Enthalpy of calcium oxalate monohydrate dehydration was found to be 32.7 kcal/mole; however, its decomposition occurs in two separate steps and the heats of activation were found to be 71.7 and 65.8 kcal/mole, respectively. The kinetic parameters for the phase transformation of theophylline are 35.4 kcal/mole for the first step and 30.7 kcal/mole for the second step. The application of the new method on cross-linked polyethylene showed that the polymer decomposes in at least three overlapping stages. Each stage has an activation energy characteristic of the process. On the other hand urea decomposition is complex and occurs in overlapping steps; each step with its characteristic heat of activation.

INTRODUCTION

In a previous communication[1] we introduced a non-isothermal method to study reactions and transformations in the solid state using thermogravimetry. The equations were based on the specific physical and chemical models involved to follow reactions

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and transformations in the solid state for each individual kinetic system using classical kinetics, and therefore deviating from the common practice of attempting to derive one universal equation applicable to all kinetic systems which can be studied using thermogravimetry. The intent was to obtain, experimentally, kinetic parameters which would be independent of such experimental variables as sample size, particle size, and heating rate, but reflecting only the chemical or physical transformation being studied. The need for such a technique was called for by several investigators during the last two decades[2-5].

The technique uses simultaneous TG–DTG curves and the analytical function of the reaction in question was specifically followed using the mass balance.

The present study was undertaken to investigate the utility and validity of these equations[1] on the kinetics of dehydration and chemical degradations of calcium oxalate monohydrate, degradation of urea and cross-linked polyethylene, as well as the kinetics of phase transformations of anhydrous theophylline. For better comparison, the thermograms used to examine the efficacy of the Gyulai and Greenhow method[6] in calculating the kinetic parameters of calcium oxalate monohydrate and theophylline[7] were used to examine the introduced method[1] in this paper.

EXPERIMENTAL

Materials

Calcium oxalate monohydrate (Fisher Scientific Co., Fair Lawn, N.J.), theophylline (Nutritional Biochemical Corp., Cleveland, Ohio) (USP), urea (Sigma Chemical Co., St. Louis, Miss.) and cross-linked polyethylene (XLPE) were used in this study. Calcium oxalate monohydrate, urea and XLPE were used as supplied. However, theophylline monohydrate was obtained by recrystallizing theophylline (USP) from double-distilled water, while anhydrous theophylline was prepared by heating theophylline monohydrate in the oven at 105°C overnight or until its X-ray diffractogram corresponded to anhydrous theophylline.

METHODS AND INSTRUMENTATION

The instrument used (Rigaku Thermoflex Analyzer, Rigaku/U.S.A., Inc., Wakefield, Mass.) is a simultaneous thermogravimetric analyzer, TGA, differential thermogravimetric analyzer, DTG, and differential thermal analyzer, DTA. It is a single furnace instrument in which the DTA cells are mounted on the weighing beam. The differential temperature and sample temperature are measured by the same thermocouple pair. The thermocouple is in direct contact with the material undergoing the scan. The DTG signal is generated with an analog system from the TGA signal. A sample trace is shown in Fig. 1.

The sample was weighed on a Cahn Electrobalance using the thermobalance platinum sample crucible as a tare so that the residual weight could be directly measured after the run. Since the sample mass ranged from 10 to 20 mg, the thermo-

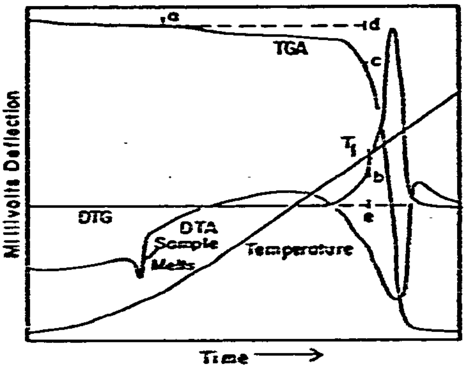


Fig. 1. Simultaneous TG–DTG thermograms for an unfilled cross-linked polyethylene from a # 14 wire, in nitrogen atmosphere, obtained from 9.00 mg as stated in the experimental conditions.

balance was calibrated for 10 mg full. The atmosphere was high purity dry nitrogen (Norwich Cylinder Co.) which was regulated at a constant flow of 160 ml/min. The sensitivity of the DTA was 500 μV. The temperature scale was 30 mV full scale with the temperature calibrated at zero voltage. Temperatures were converted to degrees centigrade by a table of electromotive force for platinal thermocouples. The heating rate was as stated in the thermogram. DTG sensitivity was 0.5. The chart speed was 10 mm/min for all runs.

The method of data collection can be illustrated using Fig. 1, which is a simultaneous TG-DTG and DTA Thermogram. On the TG curve, line a----d represents an extrapolation of the initial weight and the base to which all others are referenced. At point c, the sample was clearly losing weight and the DTG curve indicates a measurable rate. Point c can be taken as the observed sample weight, W_{obs}, at T_1. At this temperature, T_1, the rate of weight loss, $d(W_{obs})/dT$, is equivalent to the distance e----b above the DTG baseline. At a series of weight loss values, the height of the DTG curve is taken and the logarithmic term of the equation derived for the particular system is plotted versus $10^4/T$ K.

RESULTS AND DISCUSSION

The experimental applications of the previously introduced theoretical models will be demonstrated to calculate the kinetic parameters of drug desolvation, chemical degradation, and phase transformation of five compounds of different chemical structures. These compounds are calcium oxalate monohydrate, anhydrous theophylline, urea and two samples of unfilled cross-linked polyethylenes and 50% filled ethylene/propylene rubber.

Calcium oxalate monohydrate was selected because it undergoes a number of solid transformations which can be studied. It has one molecule of water incorporated in its crystal lattice, which permits the study of the rate and the mechanism of dehydration. It also undergoes degradation at high temperature in two consecutive steps, each having its own heat of activation. The first step involves the release of carbon monoxide in the temperature range 393–495°C, while the second step involves the release of carbon dioxide to form calcium oxide in the temperature range 596–768°C. On the other hand, urea exhibits chemical degradation which permits the study of the mechanisms of degradation. The third compound, anhydrous theophylline, allows the study of phase transformation of two overlapping steps. Cross-linked polyethylene permits the study of the mechanism of polymer degradation and the effect of the presence of an inert filler.

The first two mathematical models of the theoretical paper[1] will be utilized here to follow the drug desolvation, chemical degradation and phase transformations. The final non-isothermal equations for these two models can be summarized as follows.

For case Ia

solid $\xrightarrow{\Delta}$ gas

The final non-isothermal equation is

$$\log\left[\frac{-\mathrm{d}(W^t_{\mathrm{obs}})/\mathrm{d}T}{(W^t_{\mathrm{obs}})}\right] = \log\left[\frac{Z}{a}\right] - \frac{\Delta H^*}{2.303RT} \tag{1}$$

where (W^t_{obs}) is the weight observed on the thermogram at time t and temperature T, $\mathrm{d}(W^t_{\mathrm{obs}}/\mathrm{d}T)$ is the instantaneous first derivative of the weight observed with respect to temperature, a is the heating rate, ΔH^* is the heat of activation, R is the gas constant, and Z is the pre-exponential factor in the Arrhenius equation.

For case Ib

solid + $X_s \xrightarrow{\Delta}$ gas + X_s

where X_s is an inert filler and the non-isothermal equation is

$$\log\left[\frac{-\mathrm{d}(W^t_{\mathrm{obs}})/\mathrm{d}T}{(W^t_{\mathrm{obs}}) - X_s}\right] = \log\left[\frac{Z}{a}\right] - \frac{\Delta H^*}{2.303RT} \tag{2}$$

For case IIa

$(\text{solid})_1 \xrightarrow{\Delta} (\text{solid})_2 + \text{gas}$

The final equation is

$$\log\left[\frac{-\mathrm{d}(W^t_{\mathrm{obs}})/\mathrm{d}T}{(W^t_{\mathrm{obs}}) - (W^0_{\mathrm{obs}}/x)}\right] = \log\left[\frac{Z}{a}\right] - \frac{\Delta H^*}{2.303RT} \tag{3}$$

where x is the ratio M.W.$(\text{solid})_1$/M.W.$(\text{solid})_2$.

Thermal analysis of calcium oxalate monohydrate

Figure 2 shows a thermogram for calcium oxalate monohydrate generated under a nitrogen atmosphere. The thermogram shows three consecutive phase transformation steps. The first step is the dehydration of calcium oxalate monohydrate to form anhydrous calcium oxalate. The second and third steps show the chemical decomposition of calcium oxalate. The chemical decomposition in step two is the release of carbon monoxide to form calcium carbonate which in turn decomposes in the third step to release carbon dioxide to form calcium oxide. The kinetics of dehydration and chemical degradation of calcium oxalate monohydrate can be followed

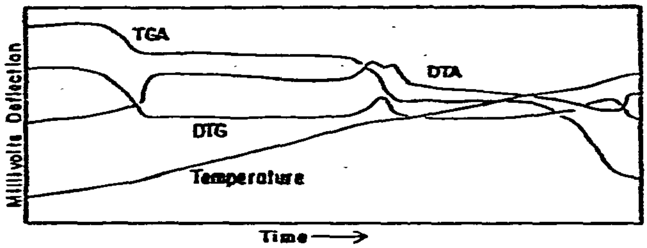


Fig. 2. Simultaneous TG–DTG thermograms from calcium oxalate monohydrate dehydration and chemical degradation, in nitrogen atmosphere, obtained from 13.6 mg as stated in the experimental conditions.

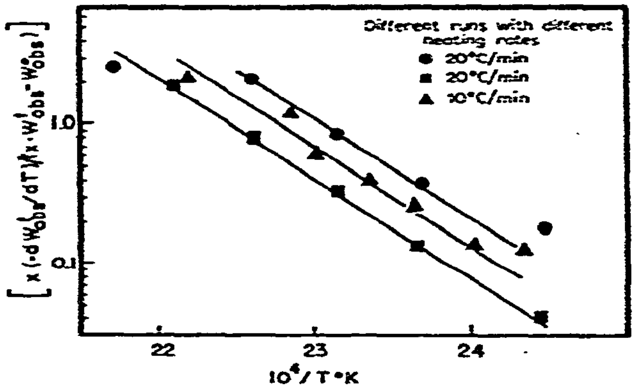


Fig. 3. Non-isothermal plots for calcium oxalate monohydrate dehydration obtained from different runs with the same sample size (13.6 ± .1 mg) but with different heating rates.

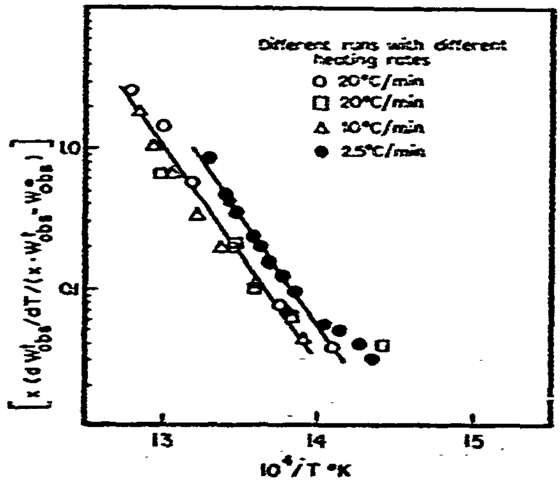


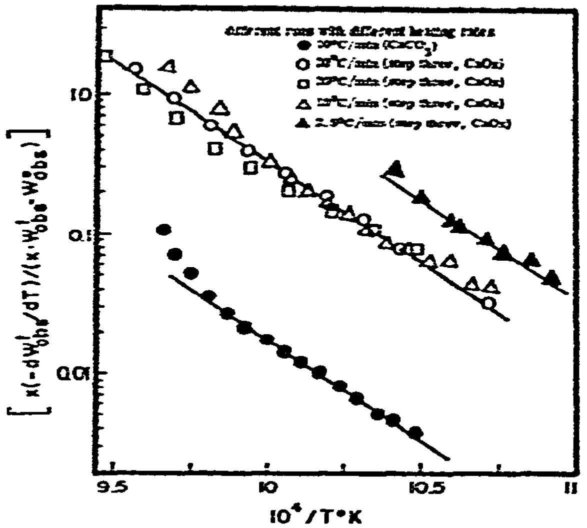
Fig. 4. Non-isothermal plots for calcium oxalate–calcium carbonate transformation (Step II), obtained from different runs with different heating rates.

using the non-isothermal equation of Case IIa [eqn. (3)]. To examine the validity of eqn. (3) and also to compare the result with that of the Gyulai and Greenhow integral method, it was decided to use the same four thermograms used[7] to evaluate the Gyulai and Greenhow integral method.

Figure 3 shows a non-isothermal plot for the kinetics of dehydration of calcium oxalate monohydrate. The plot was generated (from three thermograms obtained under different heating rates) according to eqn. (3), which predicts a linear relationship between the left-hand side logarithmic term and $1/T$ K. The plots were linear and parallel which shows the validity of eqn. (3) and that the extracted kinetic parameter is independent of the heating rate which agrees with the previous finding for methyl prednisolone Form II_b desolvation and chemical degradation[8]. The calculated heat of dehydration of calcium oxalate monohydrate equals 32.7 kcal/mole.

The chemical degradation of calcium oxalate occurs in two consecutive steps. The kinetics of calcium oxalate–calcium carbonate chemical degradation were analysed also, using eqn. (3) for different runs generated under different heating rates, and the resultant non-isothermal plot is given in Fig. 4. Figure 4 also provides linear and parallel plots which prove the validity of eqn. (3) and that the extracted kinetic parameters for the chemical degradation are independent of the experimental condition of heating rate, consistent, and reliable. The heat of activation of calcium oxalate–calcium carbonate chemical degradation which is accompanied by a loss of carbon monoxide is 71.7 kcal/mole.

Figure 5 shows the non-isothermal plot for different runs obtained under different heating rates for the calcium carbonate–calcium oxide chemical degradation.



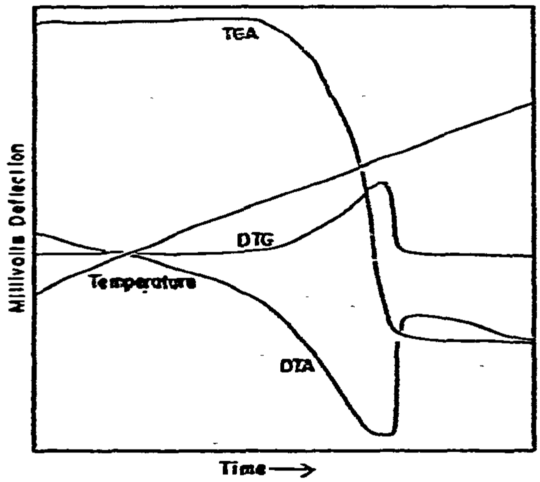
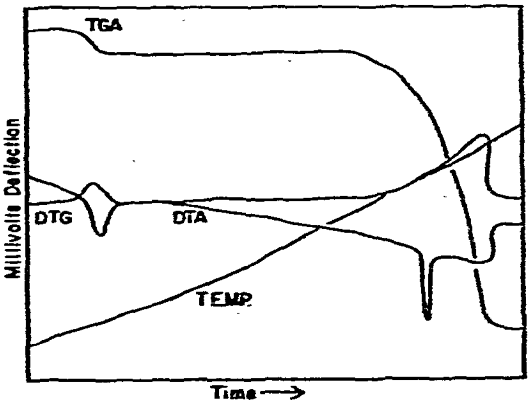


Fig. 5. Non-isothermal plots for calcium carbonate–calcium oxide transformation obtained from different runs with different heating rates of the third step of calcium oxalate decomposition as well as from pure calcium carbonate.

Fig. 6. Simultaneous TG–DTG thermograms for calcium carbonate decomposition, in nitrogen atmosphere, obtained 16.7 mg as stated in the experimental conditions.



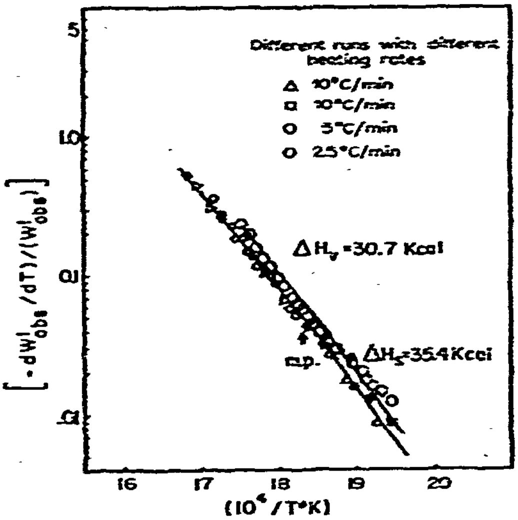


Fig. 7. Simultaneous TG–DTG and DTA thermograms for theophylline monohydrate and phase transformations, in nitrogen atmosphere obtained from 8.1 mg as stated in the experimental conditions.

Fig. 8. Non-isothermal plots for anhydrous theophylline phase transformations, obtained from different runs with the sam sample size but with different heating rates.

Four of these runs were obtained from the third step of calcium oxalate monohydrate thermograms obtained at different heating rates, while one plot was obtained from the pure calcium carbonate thermogram (Fig. 6). The non-isothermal plot shows that the data obtained from the third step of calcium oxalate monohydrate and pure calcium carbonate thermogram were linear and parallel, yielding a heat of activation of 65.8 kcal/mole. This indicates also that the calculated heat of activation is consistent and independent of the experimental conditions.

Thermal analysis of theophylline monohydrate

Theophylline monohydrate thermograms (Fig. 7) exhibit two phase transformation steps. The first step is the dehydration between 52 and 80 °C and the second step is the phase transformation between 239 and 315°C, without any chemical decomposition as the collected sublimed product does not show any difference in the UV spectra and X-ray pattern. It should be noted that the second step covers a weight loss before and after the melting point (272 ± 1 °C). Therefore, the study of the kinetics of this transformation will give the opportunity to test the validity of using eqn. (1) on overlapping steps.

The kinetics of the phase transformations of the second step of theophylline was done using eqn. (1) and the resulting non-isothermal plots are given by Fig. 8. Figure 8 shows parallel plots obtained from different runs with different heating rates which indicate that the extracted kinetic parameters are independent of the heating rates. In addition, the plots show that the phase transformation of theophylline occurs in two consecutive steps with a break in the curve at a temperature equal to the melting point (272 ± 1 °C). The enthalpies are 35.4 and 30.7 kcal/mole for the first and second linear segments, respectively. This indicates that the weight loss below the melting point gives the enthalpy of sublimation (35.4 kcal/mole) and the weight loss after the melting yields the enthalpy of vaporization (30.7 kcal/mole). This shows that eqn. (1) not only produces kinetic parameters which are independent of the experimental conditions, but also that the equation is applicable to overlapping reactions and transformations. Further applications of this technique to sublimation and vaporization were discussed by the authors in a separate publication[9].

It should be noted that the extracted enthalpy is the important parameter which is calculated from the slope of the plots. This means that the superimposability of data obtained by heating rates is not important, but parallelism is. Shifts in the thermograms should not be surprising as it should be expected that thermograms obtained at faster heating rates should shift the generated non-isothermal plot to a higher temperature. Figure 8 shows that the shifts in thermograms are in the suggested direction.

Comparisons between the Gyulai and Greenhow integration method and the new method

The thermograms used to evaluate Gyulai and Greenhow's method[7] were also used to evaluate our method[1]. Three compounds of different chemical structure were used for this purpose. These compounds were theophylline, calcium oxalate and methyl prednisolone tertiary butanol solvated form (Form II_b)[8]. The calculated ΔH^* for these compounds, using both the new method and the Gyulai and Greenhow method, were listed in Table 1. In general, the table shows that the heat of activation calculated using the Gyulai and Greenhow method varied over a wide range as a function of percentage conversion for the same runs and as a function of the experimental conditions, such as heating rates, heating rate ratios, and sample size[7]. On

TABLE 1

COMPARISON BETWEEN THE CALCULATED ΔH^* USING THE GYULAI AND GREENHOW METHOD AND THE NEW METHOD

Compound name and process	*ΔH^* (kcal/mole)*	
	Our approach[a]	*Gyulai–Greenhow method*[a]
Calcium oxalate monohydrate		
Step I (dehydration)	32.7	27.1–71.3
Step II ($CaCO_3$ formation)	71.7	37.2–75.9
Step III (CaO formation)	65.8	39–50
Theophylline		
Sublimation	$\Delta H_s = 35.4$	
Vaporization	$\Delta H_v = 30.7$	20.5–39.6[b]
Methyl prednisolone Form II_b desolvation		
Step 1	62.0	
Step 2	33.7	16.3–94.9[b]

[a] Calculated from the linear segment of the produced graph using our technique.

[b] Gyulai and Greenhow method cannot differentiate between overlapping reactions.

the other hand, the corresponding heats of activation obtained from the new technique were obtained from a linear segment of the produced graph rather than one-point determination as a function of the percentage conversion. In addition, and contrary to the Gyulai and Greenhow method, the value of the extracted heat of activation is independent of the experimental condition such as heating rate, sample size, etc. For example, the heat of activation of calcium oxalate monohydrate dehydration obtained by the use of the Gyulai and Greenhow method varies between 27.1 and 71.3 kcal/mole as a function of percentage conversion and heating rate; however, the heat of activation of dehydration of the same compound using the same thermograms obtained from the new technique resulted in 32.7 kcal/mole from all the thermograms, and independent of the experimental conditions.

The observed variation in the heat of activation calculated by Gyulai and Greenhow for the two separate steps of degradation of calcium oxalate were 37.2–75.9 kcal/mole and 39–50 kcal/mole, respectively; however, the corresponding heats of activation for the same degradations using the same thermograms obtained by the new method resulted in 71.7 kcal/mole and 65.8 kcal/mole, which are independent of the experimental conditions.

In the case of theophylline phase transformation (sublimation and vaporization) and methyl prednisolone tertiary butanol solvated form (Form II_b)[8] desolvation, there are two overlapping steps. The use of the new method yielded a non-isothermal plot for each compound, with two linear segments and from each segment a characteristic enthalpy was extracted. However, the use of Gyulai and Greenhow method[6] yielded a wide variation in the extracted kinetic parameters as a function of the percentage conversion and the experimental conditions without any indication of the presence of overlapping reactions or transformations. For example, the enthalpies of the phase transformations of theophylline extracted by the new method were found to be 35.4 and 30.7 kcal/mole for the sublimation and vaporization, respectively; however, the Gyulai and Greenhow method was not able to analyse for the two consecutive steps of theophylline phase transformation and, again, wide variation in the extracted heat of transformation was observed, as seen in Table 1.

It is apparent that the new technique provides a method which can not only analyse one-step reactions, but also consecutive overlapping reactions and transformations. In addition, the extracted heat of activation is consistent, reproducible and independent of the experimental conditions.

Use of the new method to elucidate the mechanism of degradation

The kinetic parameters of any reaction should be an intensive property and should be characteristic for that reaction. Therefore the extracted activation energy should be independent of the experiment conditions and give a clue to the mechanism of the reaction. Since the new method produces kinetic parameters which are independent of the experimental conditions, consistent, reproducible, and can analyse not only one-step reactions, but also consecutive overlapping reactions, then these parameters should give a clue to the mechanism of the reaction. For this reason, three compounds were used here to illustrate the utility of eqns. (1)–(3) in the study of the mechanism of degradation. These compounds are unfilled cross-linked polyethylene 50% filled ethylene/propylene rubber as well as urea.

The application of eqn. (1) to unfilled cross-linked polyethylene (XLPE) yielded Fig. 9. Figure 9 shows the non-isothermal plot of unfilled cross-linked polyethylene obtained from Fig. 1 and a different run. The data points were reproducible and

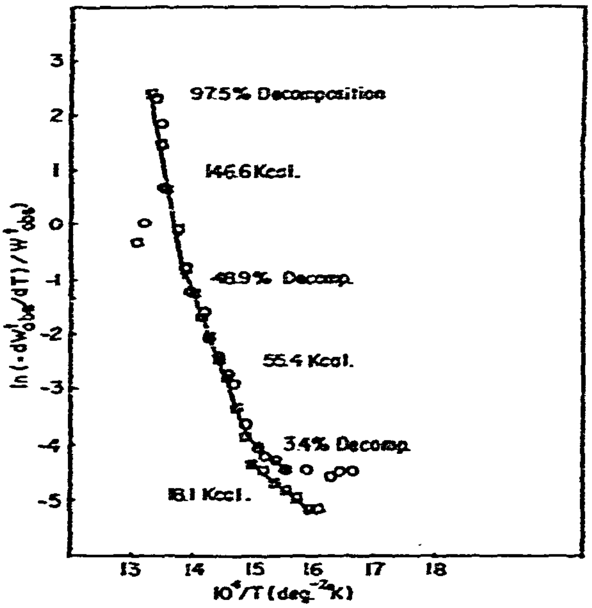


Fig. 9. Non-isothermal plots for an unfilled cross-linked polyethylene degradation obtained from two different runs.

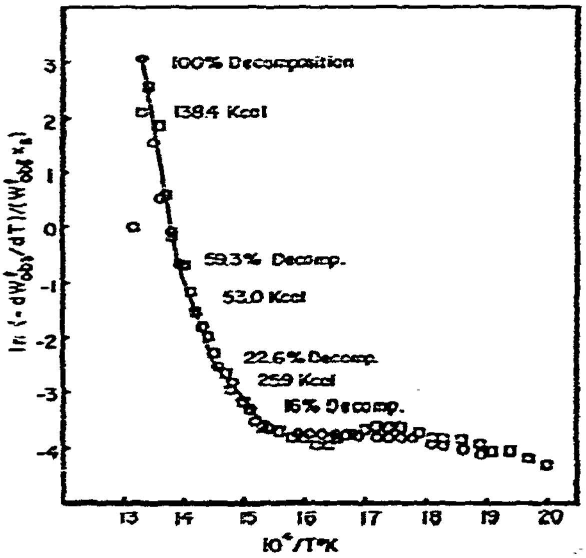


Fig. 10. Non-isothermal plots for 50% filled ethylene/propylene rubber degradation obtained from two different runs.

consistent and show that the polymer decomposes in at least three stages of increasing heat with increasing decomposition. Each of these stages has its characteristic heat of activation. This apparently supports the mechanism by which polymer degradation can proceed (either random chain scission or depolymerization). That is, frequently no single kinetic value will describe the total decomposition of most polymers over the entire decomposition range. For example, polyacrylonitrile, poly(vinylchloride)[10] and polystyrene[11] decompose in well-defined steps and present classic cases for depolymerization (chain unzipping). For polystyrene, the proof for the multistep mechanism was obtained via gel permeation chromatography[10] and pyrolysis gas chromatography[11]. However, in the case of cross-linked polyethylene, the use of the new technique provided the mechanism of the polymer degradation from a single run without the use of any additional technique.

Figure 9 shows that cross-linked polyethylene decomposes in three stages. The first stage is with a heat of activation of 18.1 kcal/equiv., which is postulated to be due to the volatilization of lower molecular weight material and cleavage of weakly held side chains. The second stage is with a heat of activation of 55.4 kcal/equiv., which is probably due to the destruction of the polymer backbone to yield volatile fragments and a char. The final stage is with a heat of activation of 146.6 kcal/equiv., which is due to the destruction of a graphite char. Figure 10 is a non-isothermal plot for ethylene/propylene rubber, 50% filled and from a second manufacturer which shows that the polymer decomposes in three overlapping steps and the heats of activation are 25.9, 53, and 138.4 kcal/mole, respectively. The values for these heats of activation are consistent and reproducible.

The effect of the inert filler generally increased the stability of the polymer but its exact effect cannot be elucidated because of the unknown identity of the filler. More work has been done by the authors on cross-linked polyethylene degradation[12].

The study of urea degradation using thermogravimetric data is a complex one

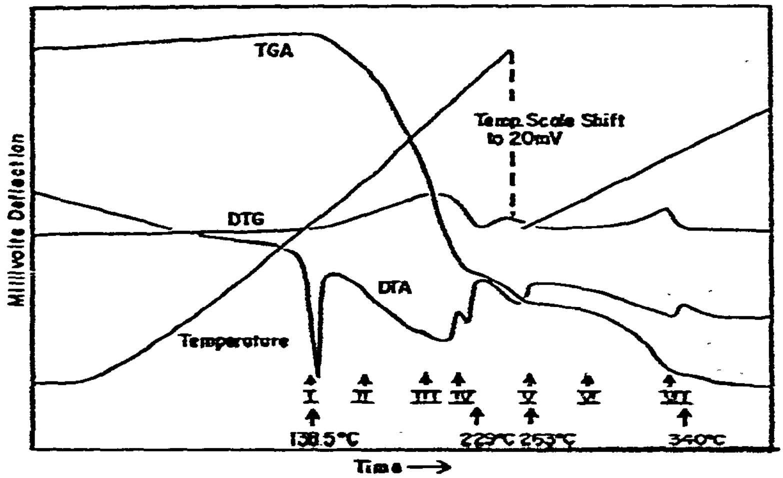
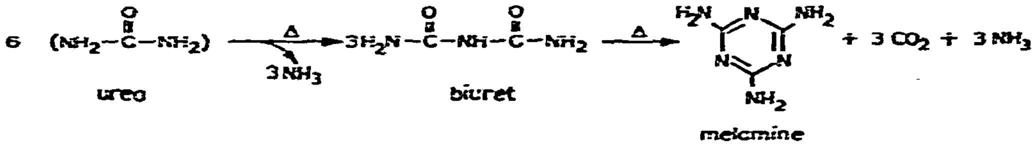


Fig. 11. Simultaneous TG–DTG thermograms for urea decomposition, in nitrogen atmosphere obtained from 8.4 mg as stated in the experimental conditions.

which cannot be done using the currently accepted kinetic equations in the literature. However, the use of the new method could isolate the consecutive steps and provide the kinetic parameters of the process involved. Figure 11 shows a simultaneous TG–DTG and DTA thermogram for urea. At point I, urea melts (132.7 °C) and starts to lose weight. This weight loss is due to the loss of NH_3 and the formation of biuret. The formation of biuret ends at point II. As the heating of the sample is continued, the biuret formed decomposes further to form melamine[13] which then solidifies at point IV. At point IV there is an exothermic reaction as indicated by the shoulder on the DTA curve which is due to the solidification. Between points IV and V, melamine melts and loses weight as seen on the DTA, TGA and DTG curves. At point V, melamine melts completely and then vaporizes between points VI and VII. The mechanism by which urea decomposes during pyrolysis is known to be as follows[13].



The kinetics of each step of urea decomposition were done using the new technique. The resulting non-isothermal plot is given in Fig. 12 which shows that urea decomposition occurs in two overlapping steps followed by physical changes (solidification and melting) and then evaporation of melamine. The arrows I–VII

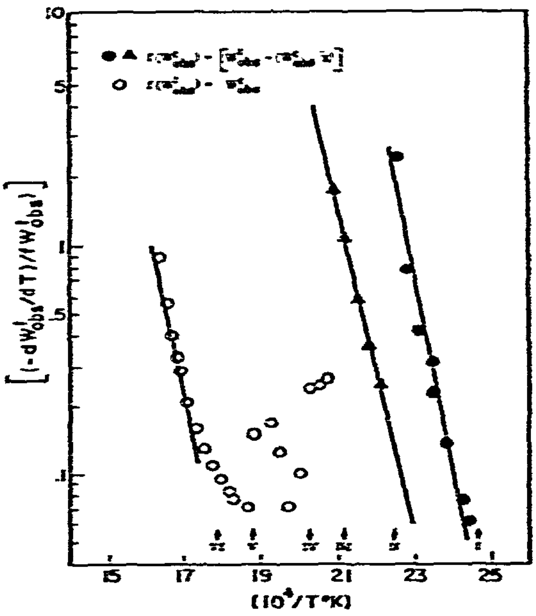


Fig. 12. Non-isothermal plots for the urea degradation obtained from Fig. 11. Arrows I–VII represent the same arrows on urea thermogram (of Fig. 11) and illustrate the stages of urea degradation as related to the kinetic analysis.

in Fig. 12 represent the arrows on the thermogram in Fig. 11. The first plot in Fig. 12 was obtained from Fig. 11 between the arrows I and II and using eqn. (3) with $x = 1.1652$, where the value of x is equal to [2(mol. wt. of urea)/mol. wt. of biuret] since two molecules of urea were needed to form one molecule of biuret. This plot is linear and has a heat of activation equal to 17.5 kcal/mole. The second plot is the non-isothermal plot for the formation of melamine obtained from Fig. 11 between arrows II and III and using eqn. (3) with $x = 2.453$, where the value of x is equal to [3(mol. wt. of biuret)/(mol. wt. of melamine)] since two molecules of biuret were needed to form one molecule of melamine. This plot is also linear [as predicted by eqn. (3)] with a heat of activation equal to 15.4 kcal/mole. Between arrows III and V in Fig. 11, there are physical changes (solidification and melting) occurring as indicated by the DTA curve. This explains the scattered points presented in the non-isothermal plot (Fig. 12) in the same temperature range. The kinetics of melamine evaporation between arrows VI and VII analysed according to eqn. (1) are given in the third linear plot in Fig. 12. The extracted heat of evaporation of melamine obtained from this plot equals 17.1 kcal/mole. From the above example, it is apparent that the careful analysis of the thermogram and the a priori knowledge of the formed decomposed products will lead to the accurate calculation of the extracted kinetic parameters.

In summary, the experimental applications of the new introduced method[1] were utilized to calculate the kinetic parameters of desolvation, chemical degradation and phase transformations of five compounds of different chemical structures. The extracted kinetic parameters for these compounds were found to be consistent, reproducible and independent of the experimental conditions such as sample size, heating rates and heating rate ratios. Therefore, the approach gives an insight into the mechanism of the reaction in question. In addition, the approach allowed the analysis of complex and overlapping reactions. In contrast, the kinetic parameters of the same compounds extracted from the same thermograms using the Gyulai and Greenhow method were not useful for mechanistic and quantitative purposes as the parameters varied as a function of the percentage conversion and the experimental conditions[7].

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