Kinetics of Thermal Degradation of Char-Forming Plastics from Thermogravimetry.   Application to a Phenolic Plastic

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Synopsis

A technique was devised for obtaining rate laws and kinetic parameters which describe the thermal degradation of plastics from TGA data.   The method is based on the intercomparison of experiments which were performed at different linear rates of heating.   By this method it is possible to determine the activation energy of certain processes without knowing the form of the kinetic equation.   This technique was applied to fiberglass-reinforced CTL 91-LD phenolic resin, where the rate law $- (1/w_0)(dw/dt) = 10^{18} e^{-55,000/RT} [(w - w_f)/w_0]^5$, nr.$^{-1}$, was found to apply to a major part of the degradation.   The equation was successfully tested by several techniques, including a comparison with constant temperature data that were available in the literature.   The activation energy was thought to be correct within 10 kcal.

Introduction

Kinetics of thermal degradation of solids have been evaluated from thermogravimetric analysis (TGA) at linear rates of temperature rise in a number of studies.   van Krevelen, van Heerden, and Huntjens[1] studied the decomposition of coal.   Freeman and Carroll[2] investigated the degradation of calcium oxalate monohydrate.   Their technique was applied to the decomposition of a styrenated polyester by Anderson and Freeman,[3] and was modified by the same authors[4] for polystyrene and polyethylene. Doyle[5] studied the degradation of a large number of plastics.   Friedman[6] investigated the decomposition of a glass-reinforced phenol-formaldehyde. A more sophisticated approach will be used in the present paper than was employed for the earlier work.

In all of the earlier studies, calculations were based on experiments which were performed at a single rate of temperature rise.   In the present paper, kinetic calculations are based on an intercomparison of experiments which were carried out at several different rates of temperature rise.

Experimental

Fiberglass-reinforced CTL 91-LD phenolic resin (a product of Cincinnati Testing and Research Laboratory) was used for this study.   The laminate
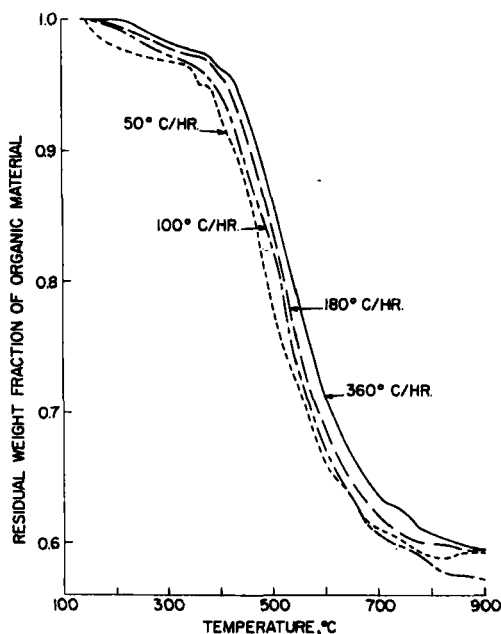
Fig. 1. TGA curves of CTL 91-LD phenolic on glass-free basis.

was prepared from resin-impregnated glass sheets that were supplied by U. S. Polymeric Chemicals, Inc. The sheets, which originally consisted of 42 wt.-% resin, were B-staged in a 200°F. oven for 1 hr. They were then cured in a 225°F. press at 100 psi for 15 min., followed by 265°F. at 100 psi for 3 hr. The cured laminate was allowed to cool to room temperature in the press, and was then post-cured in a 265°F. oven for 16 hr.

In order to prepare TGA samples, the surface layers were split off and discarded. The underlying material was converted to thin flakes by end milling under liquid nitrogen. The flakes were dried in a desiccator overnight, and were further dried by holding the sample in a porcelain crucible in the Chevenard thermobalance for 1 hr. at 100°C. just before TGA was allowed to commence. Samples lost less than 1% of their original weight during the preconditioning period.

Four 200-mg. samples of the flakes were subjected to TGA at linear heating rates of 50, 100, 180, and 360°C./hr. Degradation was carried out in a stream of dry nitrogen to maximum temperature of 900°C. After TGA was completed, the residue from each test was burned in air at 1000°C. until only glass remained. Original resin contents were found to range from 35.0 to 36.1 wt.-%.

Residual weight fractions of organic material were calculated on a glass-free basis, and are shown as a function of temperature in Figure 1. Note that the curves are displaced to higher temperatures with increased heating rate, as would be predicted from kinetic theory. Rates of weight loss are plotted as a function of time and temperature in Figure 2. Rates were
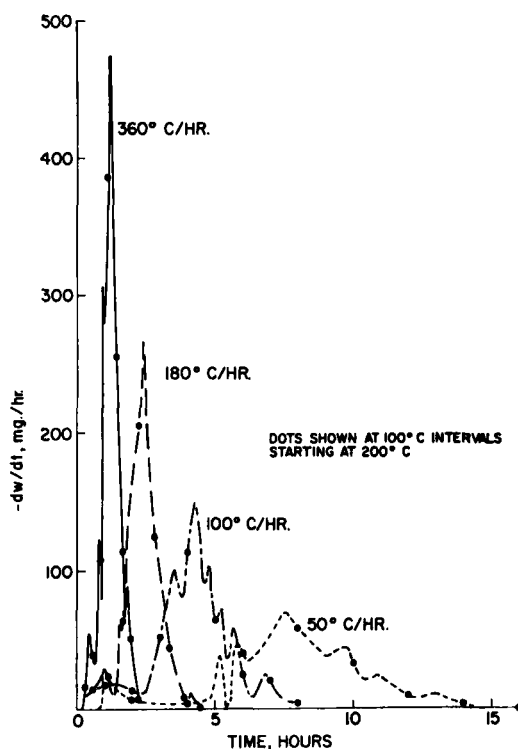
Fig. 2. Derivatives of TGA curves.

measured from enlarged graphs of Figure 1 with a Gerber derivimeter. All of the rate curves had the same general shape. Slow weight loss commenced almost immediately and continued to above 300°C. Between 300 and 400°C., the rate of loss of weight increased as the temperatures were elevated, reached a maximum in the vicinity of 500°C., and then decreased for the remainder of the heating period. Inspection of Figure 2 shows that there are a number of hills and valleys in the rate curves. Since they vary markedly from curve to curve, they are thought to be caused by scatter of the TGA data rather than indications of changes in the degradation process.

The early weight loss accounted for less than 10% of the total loss, and appeared to be associated with a different process. It was, therefore, decided to eliminate this portion from the kinetic analysis. An arbitrary initial weight of plastic was chosen from the TGA data at a temperature between 300 and 400°C. where examination of the rate curves showed that the major weight loss process appeared to begin. Although it was likely that the main degradation process started at somewhat lower temperatures, and that the early degassing process continued to higher temperatures, it was felt that the errors associated with rate measurements would be far more serious than errors caused by reasonable estimate of initial weight.
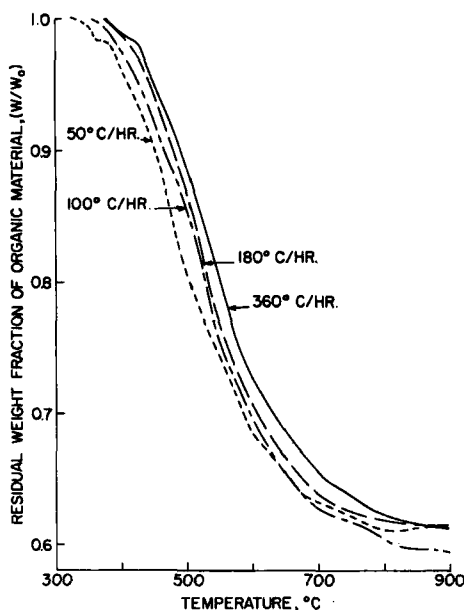
Fig. 3. TGA curves corrected for some early degassing.

Figure 3 shows residual weight fractions of organic material, with the early weight loss process eliminated.

Kinetic Analysis

The following very general kinetic equation was assumed to hold for this material.

$$(-1/w_0)(dw/dt) = Ae^{-\Delta E/RT} f(w/w_0) \qquad (1)$$

where w = weight of organic material, w_0 = original weight of plastic, t = time (in hours), A = pre-exponential factor of rate constant (per hour), ΔE = activation energy of rate constant, (in calories/mole), R = gas constant (1.987 cal./°K. mole), T = absolute temperature, and $f(w/w_0)$ = a function of the weight of organic material. Taking logarithms of eq. (1) gives

$$\ln[(-1/w_t)(dw/dt)] = \ln A + \ln f(w/w_0) - \Delta E/RT \qquad (2)$$

(fw/w_0) is assumed to be constant for constant values of w/w_0. This is comparable to assuming that the chemistry of the process is independent of temperature, and is dependent only on the instantaneous weight of the organic material. A dozen values of w/w_0 were selected, ranging from 0.675 to 0.950, at equal intervals. Values of $(1/w_0)(dw/dt)$ and T were determined for each w/w_0 for each TGA experiment. Plots of $\ln[(-1/w_0)(dw/dt)]$ versus $1/T$ are shown for each value of w/w_0 in Figure 4. The slope of each line is equal to $-\Delta E/R$, while the intercept is $\ln[Af(w/w_0)]$.

The lines of Figure 4 were obtained from least squares treatments of the data. Values of ΔE and ln $[Af(w/w_0)]$ are plotted as functions of w/w_0 in Figure 5. ΔE varies from 50 to 72 kcal./mole. The range of variation
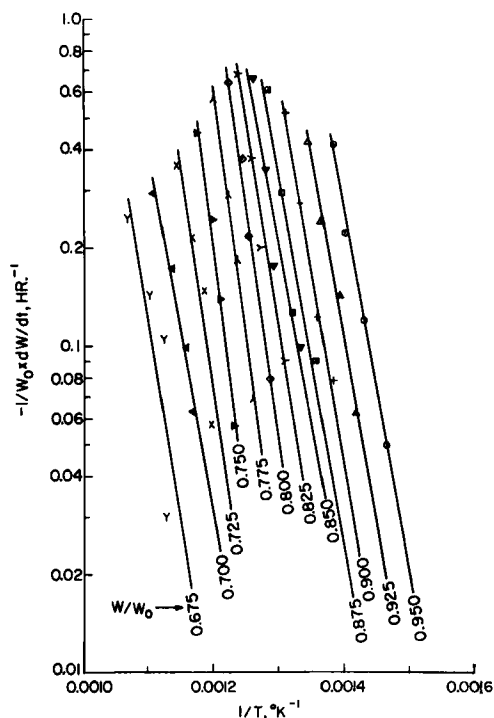

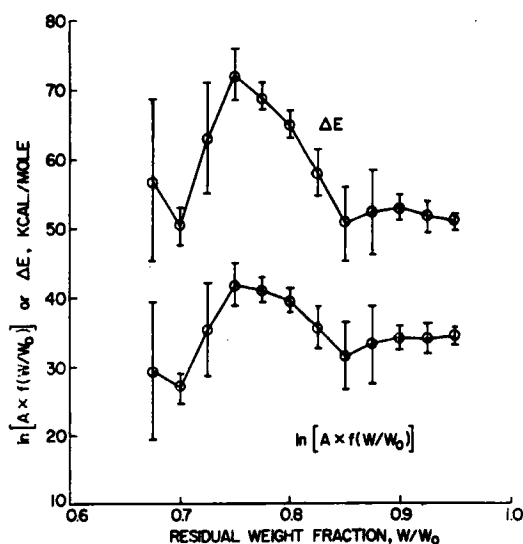Fig. 4. Arrhenius-type plots for determining kinetic parameters.

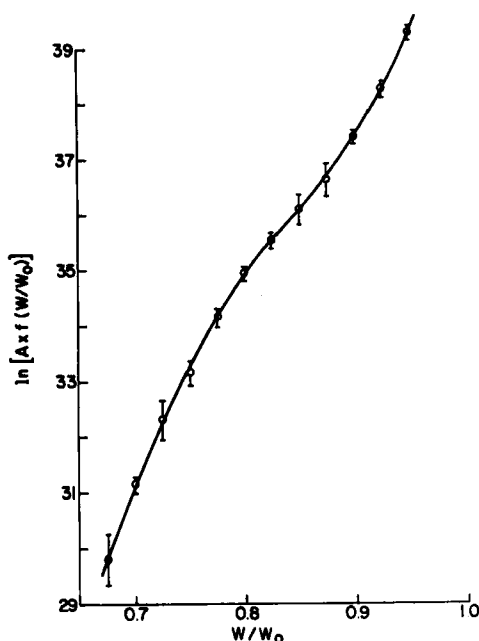Fig. 5. Kinetic parameters as a function of sample weight.

Fig. 6. Plot of ln $[Af(w/w_0)]$ as a function of sample weight.

that is associated with each point represents only the probable error of the points based on the least squares treatment. The real errors are larger. Note, however, that trends in the values of ΔE and ln $[Af(w/w_0)]$ are identical. This indicates that a positive error in A, which would make the reaction appear to go faster, is compensated for by a positive error in ΔE, which would tend to make the reaction appear to go slower. Negative errors would balance in the reverse way. Thus it appears that the kinetics of the overall process are consistent.

The 12 different ΔE's were averaged to give 57.7 kcal. Experimental parameters and the ΔE were substituted in eq. (2) to give 48 values of ln $[Af(w/w_0)]$. Average values of ln $[Af(w/w_0)]$ are plotted as a function of w/w_0 in Figure 6. The range associated with each point is the standard deviation of the average of four values. The smooth curve in Figure 6 tended to confirm that the kinetics of the overall process were consistent. (fw/w_0) was assumed to have the form

$$f(w/w_0) \; = \; [(w \, - \, w_t)/w_0]^n \eqno(3)$$

where w_t = final weight of char and n = kinetic order of the reaction. $w - w_t$ is a measure of the amount of material which is available for decomposition at any instant of time, and is a convenient mathematical form which allows the degradation to be completed when all of the original plastic is converted to char. Equation (3), or very similar forms, can be derived from theory for processes where a solid reactant is converted to a constant
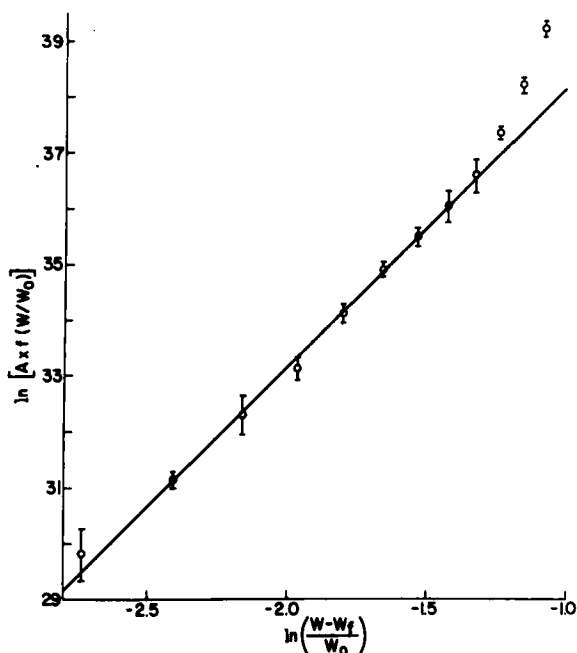
Fig. 7. Plot for the determination of A and kinetic order.

ratio of gaseous and solid products.   Multiplying both sides of eq. (3) by A and taking logarithms yields

$$\ln\,[Af(w/w_0)] \,=\, \ln A \,+\, n \ln\,[(w - w_t)/w_0] \tag{4}$$

If the assumed form of $f(w/w_0)$ is correct, then a plot of $\ln\,[Af(w/w_0)]$ versus $\ln\,[(w - w_t)/w_0]$ should give a straight line where the slope is n and the intercept is $\ln A$.   This type of plot is shown in Figure 7.   A straight line resulted for all values of the abscissa below -1.3 (equivalent to w/w_0 below 0.9).   The positive deviation at higher weights could be attributed to contributions of the early weight loss process.   In calculating values of $(w - w_t)/w_0$, it was necessary to assume a value of w_t.   Examination of Figure 3 indicated that decomposition was essentially completed at 900°C., so the convenient average value of $w_t/w_0 = 0.61$ was selected.   Calculations based on Figure 7 showed that $n = 5.0$ and $A = 5.98 \times 10^{18}$ hr.$^{-1}$. The form of the overall kinetic equation is

$$(-1/w_0)(dw/dt) \;=\; k[(w \,-\, w_t)w_0]^5 \tag{5}$$

where $k = Ae^{-\Delta E/RT}$ hr.$^{-1}$.

Tests of the Kinetic Equation

Three different tests were made on the applicability of eq. (5).   The first was an examination of Arrhenius plots for the individual runs. k's were calculated from eq. (5) by using the values of the other terms which
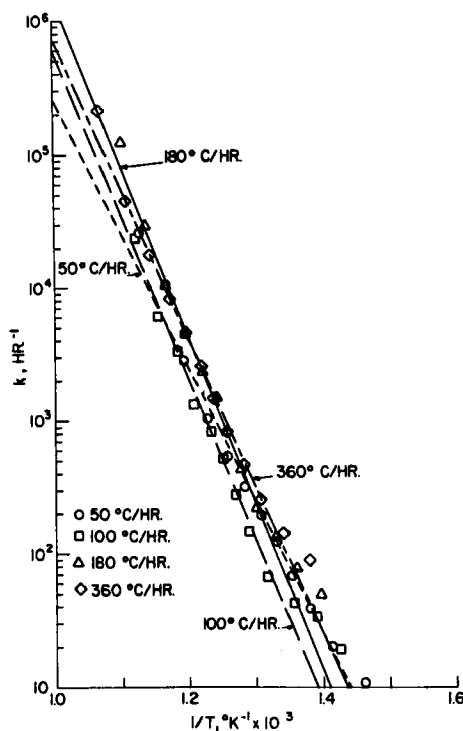
Fig. 8. Arrhenius plots of the TGA data.

were calculated earlier in the paper. w_t/w_0 was assumed to be 0.61 for all but the 100°C./hr. run, where the value of 0.59 was employed. Arrhenius plots of the four runs are shown in Figure 8. The lines are based on visual inspection of the data. The ΔE's and A's which were derived from the lines are listed in Table I. Note that the values of k are higher than

TABLE I
Kinetic Parameters Calculated by Different Methods

Rate, °C./hr.	ΔE, kcal.			A, hr.$^{-1}$	
	Kinetic analysis section	Arrhenius plot method	Second derivative test	Kinetic analysis section	Arrhenius plot method
50	Twelve values ranging	46	47		2.63×10^{15}
100	from 50 to 72 kcal.	55	66		4.79×10^{17}
180		58	70		5.13×10^{18}
360		51	56		9.55×10^{16}
Average	57.7	55[a]	60	5.98×10^{18}	10^{18a}

[a] Arrhenius plot average values were calculated from examination of all data in Figure 8.

the Arrhenius lines at the lowest temperatures. This is thought to be due to the early weight loss process, and is comparable to the deviations from linearity in Figure 6. The method of least squares was applied to all the data of Figure 8, except for the two lowest temperatures of each TGA run. ΔE was found to be 55 kcal., while A is 10^{18} hr.$^{-1}$. These values will be used for all further calculations.

The second test is based on the fact that at the maximum $(-dw/dt)$, the second derivative $(-d^2w/dt^2)$ is equal to zero. Since the heating rate is linear

$$dT/dt \; = \; \rho \tag{6}$$

where ρ = heating rate (in °C./hr.). Substituting eq. (6) in eq. (5) and rearranging gives

$$-dw/dT \; = \; (A/\rho w_0{}^4)e^{-\Delta E/RT}(w \; - \; w_t)^5 \tag{7}$$

Taking derivatives of eq. (7) yields

$$-d^2w/dT^2 \; = \; (A/\rho)[(w \; - \; w_t)/w_0]^4 \, e^{-\Delta E/RT}$$
$$[5(dw/dT) \; + \; (w \; - \; w_t)(\Delta E/RT^2)] \tag{8}$$

For $(-d^2w/dT^2) = 0$ at the maximum rate

$$5(dw/dT)_m \; + \; (w_m \; - \; w_t)(\Delta E/RT_m{}^2) \; = \; 0 \tag{9}$$

where subscript m refers to maximum rate. Equation (9) may be arranged to

$$\Delta E \; = \; 5RT_m{}^2(-dw/dT)_m/(w_m \; - \; w_t) \tag{10}$$

The four values of ΔE which were calculated from eq. (10) are listed in Table I.

The third test was to derive the individual TGA curves from eq. (5). Equation (5) was rearranged for integration to give

$$-\int_{w_0}^{w} \frac{dw}{(w \; - \; w_f)^5} \; = \; \frac{A}{\rho w_0{}^4} \int_{T_0}^{T} e^{-\Delta E/RT} \, dT \tag{11}$$

where w_0 = the arbitrary choice of initial weight of plastic and T_0 = absolute temperature at w_0.

Integration and solution for w gives

$$w \; = \; w_t \; + \; \frac{\rho^{0.25}w_0(w_0 \; - \; w_t)}{\left\{ \rho w_c{}^4 + 4A(w_0 \; - \; w_t)^4 \left[Te^{-\Delta E/RT} \; - \; T_0 e^{-\Delta E/RT_0} \; + \right.\right.}$$
$$\left.\left. \frac{\Delta E}{R} \left(\int_{v_0}^{\infty} \frac{e^{-v}}{v} \, dv \; - \; \int_{v}^{\infty} \frac{e^{-v}}{v} \, dv \right) \right] \right\}^{0.25}} \tag{12}$$

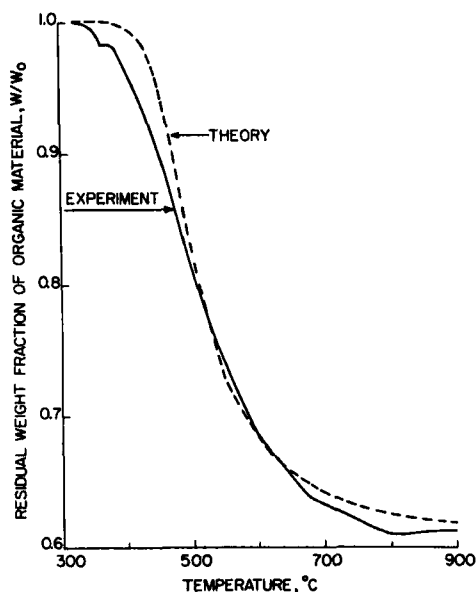where $v = \Delta E/RT$ and $v_0 = \Delta E/RT_0$.

Fig. 9. Experimental and theoretical TGA curves for the 50°.C/hr heating rate.

Solutions for the integrals which appear in eq. (12) are tabulated in several sources.[7,8] The data of Coulson and Duncanson[8] were used for this work. Figure 9 shows a typical thermogram that was derived by this technique. Note that in the lower temperature range the experimental curve shows a higher weight loss than the theoretical curve. This was expected, since the kinetic analysis and Arrhenius plots had both shown that the early weight loss process continues after temperatures which are greater than T_0.

Discussion

The various tests of eq. (5) showed that the kinetic analysis of CTL 91-LD phenolic degradation that was formulated in this paper is reasonable for a large part of the decomposition process. The main deviation between experiment and analysis occurred during early degradation, where the actual weight loss exceeded the calculated loss. The earliest weight loss can probably be attributed to desorption of absorbed gases. The resin was probably not completely cross-linked at the point where TGA started. As heating continued, further cross-linking probably occurred, and further weight loss could be attributed to the evolution of some condensation products. Since degradation probably started before crosslinking was completed, there is probably no simple value for w_0, in the way that it was used. Examination of Figure 9 shows that a slightly lower w_0 would make the theoretical curve fit the experiment better. It is altogether reasonable, when one considers the argument that was presented above, that the effective w_0 be lower than the chosen value. It is also not surprising that the

theoretical weight at 900°C. is slightly higher than the experimental figure. Adjustments could probably be made in the choice of both w_0 and w_f, so that very accurate theoretical TGA curves would result, except for the very earliest weight loss processes.

A fifth-order weight dependence is unusual for polymer degradation. Of course, order does not mean the same thing in this type of process as it does for a gas or a solution. Since this resin is a highly crosslinked material, it is likely that the high order was associated with a rather complex mechanism which occurred in the solid state. Note, however, that a pre-exponential factor of about 3×10^{14} sec.$^{-1}$ and an activation energy of 55 kcal. are not unusual for some thermoplastics.

Inspection of the low temperature end of the TGA curves showed that very low activation energies could be attributed to that part of the decomposition. In the earlier kinetic analysis,[6] this author studied TGA experiments which were performed only at 180°C./hr. on a sample where the resin content had not been determined. Since that analysis covered temperatures ranging between 404 and 524°C., it is reasonable that an activation energy of 15 kcal. was calculated. Madorsky and Strauss[9] investigated the thermal degradation of the non-reinforced phenolic in vacuum and at constant temperature. Rate measurements at 7% degradation at 355 and 380°C. were used by these authors to estimate the activation energy of degradation as 18 kcal., in agreement with the previous study.[6] Nevertheless, the present author feels that the early degradation should be studied further by methods which would yield reproducible rates.

Madorsky and Strauss carried out a few experiments to comparatively high extents of reaction, and it is possible to compare their data with that of the present work. Total per cent of volatilization was reported as a consequence of heating for a given length of time at 420, 500, and 800°C. To compare data, eq. (5) was integrated to give

$$w = w_f + \frac{w_0(w_0 - w_f)}{[w_0{}^4 + 4 \times 10^{18}te^{-55,000/RT}(w_0 - w_f)^4]^{0.25}} \tag{13}$$

These workers determined elemental analyses for several samples which were pyrolyzed to various extents of decomposition at various temperatures. After 5 min. of pyrolysis at 1200°C. a residue was produced with 51.6% of the original sample weight where 99.2% of the residue was carbon. Complete conversion to carbon would be expected at a residue weight of about 51%. Since the present samples had reached rather constant weight after the comparatively lengthy heatings to 900°C., it is likely that they had been converted to pure carbon. Elemental chemical analysis of these chars would have been desirable. Differences in the w_f's could readily be caused by different batches and differences in sample preparation. Although eq. (13) ignored early weight loss and w_0 was defined on a different basis than that by which the equation was derived, it was felt that the calculation would still be meaningful. w_f is probably the most

important parameter for this calculation so long as the extent of reaction is great enough for most or all of the early weight loss gases to be evolved. The three runs that were chosen seemed to qualify reasonably well on this basis. The results of comparison are listed in Table II. The agreement between the results is excellent and lends further support to the present kinetic analysis.

The kinetic analysis technique that was employed in this paper has several advantages. By its use it was possible to calculate an activation energy for the main degradation process without any knowledge of the form of the kinetic equation. It was also useful for the purpose of deriving a semiempirical rate law, which would be difficult to arrive at by other methods. This method could also serve as a check for systems where the rate laws seem to be so simple that TGA experiments would only be carried out at one rate of heating under normal circumstances.

TABLE II
Comparison Between Results of the Present Work with Experiments of Madorsky and Straus

Temperature, °C.	Heating time, min.	w/w_0	
		Observed	Calculated
420	130	0.84	0.87
500	30	0.72	0.71
800	5	0.56	0.54

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Résumé

On a mis au point une méthode rélévant les équations de vitesses et les paramètres cinétiques qui décrivent la dégradation thermique de plastiques à partir de données TGA.

La méthode est basée sur la comparison des expériences obtenues à diverses vitesses linéaires d'échauffement   Cette méthode permet de déterminer l'énergie d'activation de certains processus, sans en connaître la forme de l'équation cinétique.   On applique cette technique à la résine phénolique renforcée avec des fibres de verre CTL 91-LD dont l'équation de vitesse: $- (1/w_0)(dw/dt) = 10^{18} e^{-55,000/RT} [(w - w_f)/w_0)]^5$, hr^{-1}, a été trouvée applicable à la majorité des dégradations.   L'équation a été vérifiée à l'aide de plusieurs techniques, y compris une comparaison avec des données d'expériences à température constante, trouvées dans la littérature.   On démontre que l'énergie d'activation est correcte à moins de 10 kcal près.

Zusammenfassung

Ein Verfahren zur Ermittlung der Geschwindigkeitsgesetze und kinetischen Parameter beim thermischen Abbau plastischer Stoffe aus TGA-Daten wird angegeben. Das Verfahren beruht auf dem wechselseitigen Vergleich von Versuchen bei verschiedener linearer Erhitzungsgeschwindigkeit. Mit dieser Methode kann die Aktivierungsenergie gewisser Prozesse ohne Kenntnis der Form der kinetischen Gleichung bestimmt werden. Das Verfahren wurde auf glasfaserverstärktes CTL 91-LD-Phenolharz angewendet, das im Hauptteil des Abbaues dem Geschwindigkeitsgesetz $-(1/w_0)(dw/dt) = 10^{18} e^{-55,000/RT}[(w - w_f)/w_0]^5$, hr^{-1} gehorcht. Die Gleichung konnte mit Erfolg nach mehreren Methoden überprüft und mit Literaturwerten bei konstanter Temperatur verglichen werden. Die Aktivierungsenergie dürfte mit einer Genauigkeit von 10 kcal korrekt sein.