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COMPARISON OF ISOTHERMAL AND DYNAMIC METHODS FOR THE DETERMINATION OF ACTIVATION ENERGY BY THERMOGRAVIMETRY

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Several dynamic methods for estimating activation energies have been developed. This development has arisen largely as a matter of convenience and the desire to minimize analysis time. While these methods generally afford values which are somewhat similar, the agreement among values from various methods is never outstanding. Further, the values obtained are often, at best, only approximations of the values obtained by the traditional isothermal approach. To better ascertain the utility of dynamic methods for the determination of activation energies, the activation energy for the thermal degradation of a standard vinylidene chloride/methyl acrylate (five-mole percent) copolymer has been generated by a variety of methods. The degradation of this polymer is an ideal reaction for evaluation of the various methods. At modest temperatures (<200°C), the only reaction that contributes to mass loss is the first order evolution of hydrogen chloride, i.e., there is only one significant reaction occurring and it is not impacted by competing processes. The best values (most reproducible; best correspondence to values obtained by titrimetry and other methods) are those obtained by plotting the natural logarithm of rate constants obtained at various temperatures *vs.* the reciprocal of the Kelvin temperature. Various dynamic methods yield values which are less reproducible and which approximate these values to a greater or lesser degree. In no case is the agreement good.

Keywords: *activation parameters, kinetics, kinetic parameters, polymer degradation, thermogravimetric methods*

Introduction

Thermogravimetry is a useful, convenient method for the study of a variety of decomposition processes for a range of materials [1]. Often kinetic data are extracted from a plot of mass loss *vs.* time or temperature. Reliable information may be obtained for well-defined single processes in which the evolution of a well-characterized gaseous product or products reflects the rate of decomposition. In many cases, decomposition does not correspond to a single, well-defined event. Often many processes occur simultaneously. In the cases, the ‘kinetic data’ obtained are characteristic of no fundamental process and are of limited value [2]. The most appropriate way to obtain reliable kinetic data is to monitor mass loss *vs.* time to obtain rate constants at several different temperatures [3]. Several repetitions at each temperature provides a good reflection of the uncertainty in the values for the rate constants obtained. The enthalpy of activation, $\Delta H^{\ddagger}$, may then be obtained from the slope of a plot of $\ln\frac{k}{T}$ *vs.* $\frac{1}{T}$ where k is the rate constant at a particular Kelvin temperature, T. The slope of this plot is $-\Delta H^{\ddagger}/R$ where R is the gas constant, 8.3145 J mol^{-1}. Because this procedure is tedious and time-consuming a number of variable temperature techniques for determining activation energies have been developed [4, 5]. While these methods afford convenience and speed in generating activation values, the reliability and utility of the values obtained are generally lower than those obtained by the more laborious isothermal technique [3]. While it is clear that approximations of activation energy may be obtained by a variety of approaches, the relative merits of the various techniques have not been directly compared for a well-defined process free of complications that often plague measurements of this kind. A model reaction suitable for testing the relative suitability of various approaches for the determination kinetic parameters is the thermal degradation of a standard vinylidene chloride/methyl acrylate (5 mol%) copolymer. At moderate temperatures (< 200°C) the polymer undergoes thermally-induced dehydrochlorination. In fact, this is the primary degradation process which accompanies processing of the polymer. The early stage dehydrochlorination is uncomplicated by interfering processes, i.e., the only product observed by evolved gas analysis is hydrogen chloride, and sample mass loss is directly reflective of the extent of degradation [16].

Results and discussion

Because of their importance in the barrier plastic packaging industry the thermal degradation of

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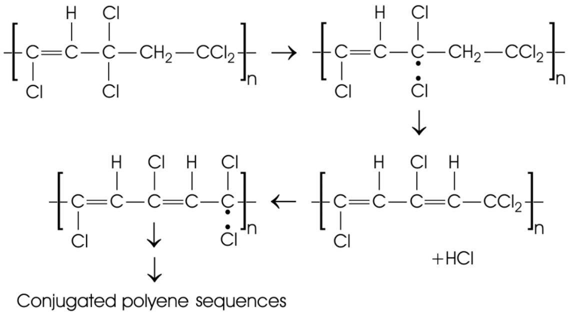
vinylidene chloride polymers has been extensively studied [16–22]. The principal process occurring at modest temperatures is degradative dehydrochlorination. Thermal homolysis of an allylic carbon–chlorine bond generates a tight carbon chlorine radical pair. The chlorine atom most generally abstracts an adjacent hydrogen atom to extend the unsaturation by one unit, to generate an allylic dichloromethylene group, and to propagate the dehydrochlorination reaction. This is outlined below in Sch. 1.



Scheme 1 Mode of degradation of vinylidene chloride polymers

This reaction is well-suited for study by thermogravimetry since the only process occurring at modest temperatures (120–200°C) is the loss of hydrogen chloride, i.e., no other volatile products are formed at these temperatures. Therefore, the rate of change of sample mass accurately reflects the rate of degradation. Both the initiation and propagation phases of the degradation are apparent in thermograms for decomposition at constant temperature. These regions are even more obvious in a plot of $\ln\left(\frac{w_\infty - w_0}{w_\infty - w_t}\right)$ *vs.* time where w_∞ is the mass of the sample at infinite time (t_∞) taken as that mass that remains after 37.62% of the initial vinylidene chloride component mass (corresponding to the complete loss of one mole of hydrogen chloride per vinylidene chloride unit in the polymer) has been lost; w_0 is the mass at time zero (t_0), i.e., the time at which the first data point was recorded and w_t is the mass at any time t, during the run. This is illustrated in Fig. 1.

Rate constants for both initiation (k_i) and propagation (k_p) may be obtained from the appropriate linear portions of this plot. This is illustrated in Figs 2 and 3 in which portions of the data presented in Fig. 1 are replotted. It might be noted that an excellent least squares fit is obtained in both cases. In practice, data for multiple runs are plotted and the average reported as the rate constant. This permits a ready assessment of the uncertainty in the value for the rate constant. Reproducibility is typically excellent. Determination of rate constants at several temperatures provides the

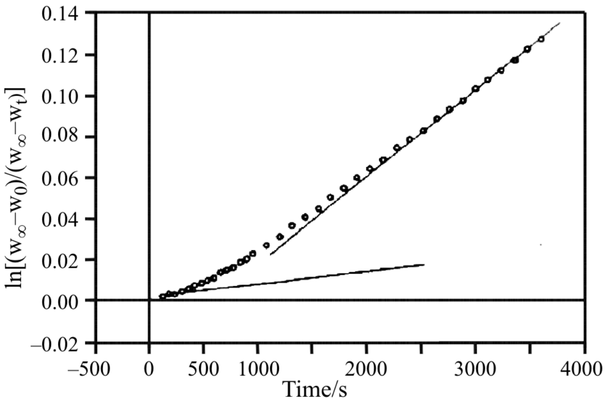


Fig. 1 Thermal degradation of a typical vinylene chloride polymer at 180°C

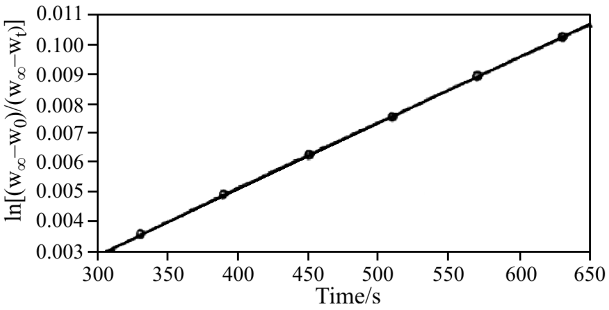


Fig. 2 Initiation rate constant (k_i) for the thermal degradation of typical vinylidene chloride polymer at 180°C

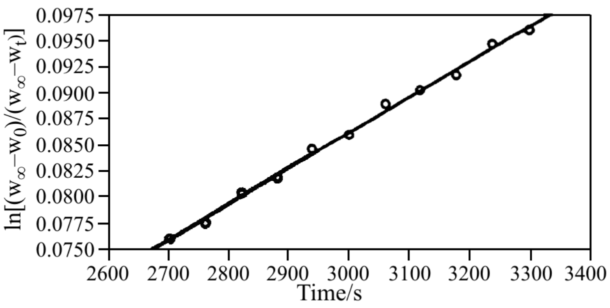


Fig. 3 Propagation rate constant (k_p) for the thermal degradation of typical vinylidene chloride polymer at 180°C

Table 1 Rate constants for the thermal degradation of a vinylide chloride/methyl acrylate (five mole percent) copolymer

$k_i \cdot 10^5$/s$^{-1\ a,c}$	$k_p \cdot 10^5$/s$^{-1\ b,c}$	Temperature/°C
1.56±0.05	2.24±0.10	170
3.32±0.16	4.15±0.01	180
6.26±0.12	8.91±0.09	190
14.56±0.58	17.75±0.16	200

[a] Rate constant for the initiation of degradation
[b] Rate constant for the propagation of degradation
[c] Averages of three determinations accompained by the average deviation

Table 2 Activation parameters for the degradation of a vinylidene chloride/methyl acrylate (five mole percent) copolymer

Initation of degradation			Propagation of degradation		
$\Delta H_i^\ddagger$/kJ mol^{-1a}	E_{ai}/kJ mol^{-1a}	$\Delta S_i^\ddagger$/J mol^{-1} °C^{-1} (200°C)^b	$\Delta H_p^\ddagger$/kJ mol^{-1a}	E_{ap}/kJ mol^{-1a}	$\Delta S_p^\ddagger$/J mol^{-1} °C^{-1} (200°C)^b
123.85	127.65	–60.46	117.74	121.55	–71.80

[a] Based on the uncertainly in the values for rate constants and the temperature control (±0.2°C) possible with the TG unit, the estimated uncertainty in activation values is less than 2.1 kJ mol^{-1}.

[b] Calculated from the expression: $\Delta S^\ddagger/R = \ln(k) - 23.760 - \ln(T) + \Delta H^\ddagger/R$ using the experimental activation enthalpy.

Table 3 Values for the Arrhenius activation engergy for propagation of the thermal degradation of a vinylidene chloride/methyl acrylate (five mole percent) copolymer determined by various methods

Methods	Parameters plotted	Correlation coefficient	E_a/kcal mole^{-1}	Uncertainty
Isothermal	$\ln(k)$ *vs.* $1/T$	0.9993	29.05 (123.43)^b	±0.42
Flynn–Wall–Ozawa^a	$\log\beta$ *vs.* $1/T$	0.9908	30.50 (127.61)^b	±1.10
Constant Reaction Rate^a	$\ln(d\alpha/dt)$ *vs.* $1/T$	0.9905	30.71 (128.49)^b	±1.59
Dynamic Heating Rate^a	$\ln(Hr/T^2)$ *vs.* $1/T$	0.9504	30.24 (126.52)^b	±1.38

[a] For a detailed description of this method see: [13]; [b] (kJ mol^{-1})

data needed for the construction of a plot of $\ln\left(\frac{k}{T}\right)$ *vs.* $\frac{1}{T}$ (where k is the rate constant and T is the corresponding Kelvin temperature) and the extraction of the enthalpy of activation ($\Delta H^\ddagger$). The Arrhenius activation energy, E_a, may be obtained similarly from a plot of $\ln(k)$ *vs.* $\frac{1}{T}$. Values for an activation energy may also be obtained by a variety of variable temperature techniques.

To determine the utility, i.e., the relative ‘goodness’, of the various approaches for the determination of activation energy, the thermal degradation of a standard vinylidene chloride/methyl acrylate (5 mol%) copolymer has been examined by thermogravimetry. In particular a direct comparison between three of the most commonly used variable temperature techniques and the more reliable isothermal approach has been possible. Rate constants for the degradation at several temperatures are displayed in Table 1.

The corresponding activation parameters are contained in Table 2. In addition, the Arrhenius activation energy for propagation of the degradation has also been determined using three variable temperature techniques. The values obtained are displayed in Table 3. It can be seen that 1.) all the variable temperature methods give rise to poorer data fits (poorer correlation coefficients) than does the isothermal method 2.) the uncertainty in the value for the activation energy obtained from the variable temperature methods is generally greater than that for the value obtained from the isothermal method and 3.) the value for the activation energy generated from the variable temperature techniques is in every case greater than that obtained using the isothermal method. These observations are in good agreement with previous suggestions and provide a good reflection of the utility of the various methods for a ‘best case’ situation [3–22].

Conclusions

The degradation of vinylidene chloride polymers represents an ideal reaction for study using thermogravimetric techniques. Degradation corresponds to a single, well-defined process – the elimination of hydrogen chloride – such that mass loss as a function of time provides a direct reflection of the rate of degradation. Because this process is so well-behaved, it provides a good vehicle for an evaluation of the relative merits of various approaches to the extraction of kinetic parameters from thermogravimetric data. It has been demonstrated that the isothermal method which involves the determination of rate constants at several temperatures and the construction of a plot of $\ln(k)$ *vs.* $\frac{1}{T}$ for the extraction of the Arrhenius activation energy is clearly superior to any of several variable temperature approaches for obtaining the same quantity.

Acknowledgements

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