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APPLICATION OF SCANNING CALORIMETRY TO THE STUDY OF CHEMICAL KINETICS

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ABSTRACT

The principles involved in the simple homogeneous decomposition of a pure compound in a condensed phase are discussed, and it is shown that the reaction order for such a system must be one. Any deviation of the reaction order from one indicates a complex reaction, and a true activation energy for such a system cannot be obtained by any presently available thermal method. Thermochemical methods for the determination of activation energies are compared, and a new method is presented.

SYMBOLS USED

A, A_p^*	reactant and its activated complex
a	proportionality constant
α	proportionality constant including heat of reaction $\equiv am_0Q$
B	linear heating rate in degrees·sec^{-1}
b	DSC deflection from baseline in mm
$\dot{b}$	db/dt, the slope of the DSC curve at any point
C	concentration of active mass
E	activation energy
k	rate constant
m	weight of reactant
m_0	sample weight in g
n	reaction order
φ	linear heating rate, Kissinger notation (= B in our notation)
Q	heat of reaction, cal·g^{-1}
p	an integer
q	heat evolved
$\dot{q}$	energy evolution rate
R	gas constant, 1.9872 cal·mole^{-1}·degree^{-1}
T	absolute temperature
T_m	absolute temperature at the DSC curve maximum
t	time in seconds
x	fraction decomposed

$\dot{x}$	decomposition rate, dx/dt
x_m	degree of decomposition at the curve maximum
Z	preexponential in the Arrhenius equation

INTRODUCTION

Thermal methods, such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are becoming increasingly popular for the determination of kinetics constants. Unfortunately, there appears to be a considerable amount of confusion concerning the interpretation of the experimental data and the importance of various experimental factors. In this paper we particularly wish to consider the principles involved in the application of the DSC to studies of the decomposition of pure, condensed-phase systems in which the reaction occurs homogeneously and without dilution of the reactant by the reaction products.

The usual starting point for the analysis of the experimental data is the classical rate equation*

$$-dc/dt = kc^n \tag{1}$$

Obviously, for the systems being considered here, c is constant throughout the reaction, and Eqn. (1) reduces to nonsense. Under these conditions the reaction rate is simply proportional to the number of activated complexes present at any instant, and this in turn is directly proportional to the amount of reactant present. Thus for any reaction of the form

$$pA \rightarrow A_p^* \rightarrow \text{products} \tag{2}$$

where the products are volatile or immiscible with A, the rate equation assumes the simple form

$$-dm/dt = km \tag{3}$$

Here k has its usual significance in transition-state theory, but for our purposes it will suffice to interpret k in terms of the Arrhenius equation,

$$k = Ze^{-E/RT} \tag{4}$$

The point we wish to emphasize is as follows: if the decomposition of a pure liquid or solid conforms to our model, the reaction of necessity is first order in m — that is, $n = 1$; if $n \neq 1$, the reaction is complex. In the latter case n may assume noninteger values, or may even vary as the reaction proceeds. Among the possible causes of complex reactions are catalysis or inhibition by products, dilution of the reactant by reaction products, or a mechanism involving nonhomogeneous reactions such as might occur *via* the formation and growth of nuclei. The last is particularly common in the decomposition of pure solids; obviously, neither Eqn. (1) nor Eqn. (3) applies in such cases, and attempts to interpret such reactions by means of these equations are futile.

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* For a glossary of symbols used, see pp. 1 and 2.

In applying thermal methods to the study of the kinetics of the decomposition of a pure liquid or solid, then, there are two important questions to be considered: does the reaction conform to the assumed model, and, if so, how can we extract E and Z from the data?

Thus far the latter question has been emphasized by most investigators, and a number of methods have been proposed for extracting kinetics constants from DTA data. Especially prominent is Kissinger's[1] method for determining E from multiple DTA runs. Reed *et al.*[2] considered the DTA thermal resistance problem and concluded that Kissinger's method would be inaccurate. They demonstrated a considerable degree of inaccuracy for the method in the determination of E and Z for the decomposition of benzenediazonium chloride. They appear, however, to have missed the greatest potential source of inaccuracy in the method. Kissinger's Eqn. 9 relates the various parameters at the DTA peak as follows:

$$E\varphi/RT_m^2 = Zn(1-x)_m^{n-1}\,e^{-E/RT_m} \tag{5}$$

Kissinger then stated: "The product $n(1-x)_m^{n-1}$ is not only independent of φ (the heating rate), but is very nearly equal to unity." This can be true only when n is close to 1 — *i.e.*, when the reaction conforms to the model being considered here. If the reaction is complex, x_m will vary with T_m at different heating rates, as shown in Table I for two decompositions of different complexity. Recognizing this fact, Kissinger cautioned that the method should be used for simple decomposition reactions only; however, many unsuccessful attempts are still being made to apply the method to the most complex systems.

TABLE I

RELATIONSHIP BETWEEN HEATING RATE, B, AND FRACTION DECOMPOSED AT THE CURVE MAXIMUM, x_m, FOR HMX AND RDX

B (°K·sec^{-1})	x_m	
	HMX	*RDX*
0.04167	0.385	—
0.08333	0.315	0.629
0.16667	0.295	0.622
0.33333	0.415	0.600
0.66667	0.470	0.640

Danes and Ponec[3] appear to have developed independently a method similar to that presented by Kissinger; however, they made their plots at constant fraction decomposed. Ozawa[4] adapted the method to the TGA technique, considering the fraction decomposed as a function of T for different heating rates. Unfortunately, it is doubtful that much can be gained by the more sophisticated treatment of the data because, if the fraction decomposed at T_m is not constant with different heating rates, the reaction must be complex. If the reaction is complex, the system does not conform to the model upon which the derivations were based, and accurate results cannot be obtained. The accuracy that can be expected from any of the related methods must be a function of the degree of complexity of the reaction.

It can be seen from results presented in ref. 2, and from results to be presented here, that the unmodified Kissinger method, applied to organic decompositions for which multiple reaction routes are possible, tends to give low results. *Reaction order should be studied before an attempt is made to derive the kinetics constants.* In what follows our principal purpose is to describe a procedure, applicable to the DSC, which permits one to determine whether a decomposition reaction conforms to the model represented by Eqn. (3), and, if it does, to obtain best estimates of the kinetics constants, all from an analysis of a single DSC curve.

We start with an alternative form of Eqn. (1), namely,

$$\dot{x} \equiv \mathrm{d}x/\mathrm{d}t = k(1-x)^n \tag{6}$$

At any temperature we have

$$\dot{q} \equiv \mathrm{d}q/\mathrm{d}t = -Q\mathrm{d}m/\mathrm{d}t = Qm_0\mathrm{d}x/\mathrm{d}t = m_0Q(1-x)^n k \tag{7}$$

In the case of the DSC, the deflection of the curve from the baseline is proportional to the rate of energy evolution, the proportionality constant being independent of temperature. Therefore,

$$b = a\dot{q} = am_0Q(1-x)^n k = \alpha(1-x)^n k = \alpha\dot{x} \tag{8}$$

From the definitions we have

$$x(t_i) = q(t_i)/Qm_0 = \frac{1}{Qm_0}\int_0^{t_i} \dot{q}\mathrm{d}t = \frac{1}{\alpha}\int_0^{t_i} b\mathrm{d}t \tag{9}$$

from which it is readily apparent (letting $t_i \to \infty$) that α is simply the total area under the curve. We note in passing that Eqns. (8) and (9) already permit one to determine k as a function of t or T, for any assumed value of n, from a single DSC run[5,6], a point we will return to later.

Now Eqn. (8) can also be written

$$b = \alpha Z(1-x)^n \mathrm{e}^{-E/RT} \tag{10}$$

Differentiating with respect to time and solving for E we have

$$\begin{aligned}\dot{b} \equiv \mathrm{d}b/\mathrm{d}t &= \alpha Z[(1-x)^n \mathrm{e}^{-E/RT}BE/RT^2 - \mathrm{e}^{-E/RT}n(1-x)^{n-1}\dot{x}] \\ &= b[BE/RT^2 - nb/\alpha(1-x)]\end{aligned} \tag{11}$$

and

$$E = \frac{RT^2[\dot{b}+nb^2/(1-x)\alpha]}{bB} \tag{12}$$

Since b, $\dot{b}$, and x are readily determined as a function of t or T, Eqn. (12) again makes it possible to calculate an activation energy at any temperature on a DSC curve from information that can be determined directly from the curve and an assumed value of n. This ability can be of considerable help in the study of decomposition mechanisms. Of greater importance, however, is the fact that n and E can be obtained simultaneously from a least-squares fit of Eqn. (12) in the form

$$(1-x)\dot{b}/b^2 = (1-x)BE/bRT^2 - n/\alpha. \tag{13}$$

If $(1-x)\dot{b}/b^2$ is plotted against $(1-x)/bT^2$, the slope is BE/R and the intercept is $-n/\alpha$.

At the peak maximum $\dot{b} = 0$ and Eqn. (12) reduces to

$$E = \frac{RT_m^2 nb}{B(1-x_m)\alpha} \tag{14}$$

This form, of course, is useful only when n is known with some confidence. In particular, in the decomposition of a pure liquid or solid, if $n \neq 1$, the derived values of E and Z are, at best, highly suspect.

EXPERIMENTAL PROCEDURE FOR APPLICATION OF EQNS. (12)–(14)

A. — Weigh a sample (if Q is to be determined) and run a regular DSC curve, indicating DSC range setting and temperature programming rate.

B. — Measure α, the total area between the curve and the baseline. If b is measured in mm and B is recorded in °C·sec^{-1}, the dimensions of α must be mm·sec. The fraction decomposed at T_i is

$$x(T_i) = \text{Area to } T_i/\alpha \tag{15}$$

The rate at T_i is given by

$$\dot{x}(T_i) = b(T_i)/\alpha \tag{16}$$

C. — Measure the slope at T_i, $\dot{b}(T_i)$, by constructing a tangent at T_i.

D. — Plot the data in the form specified by Eqn. (13). If the points lie on a straight line for an extended range of values of x, determine E and n from a least-squares calculation, using only those points within the region of linearity. Alternatively it is possible to test whether or not the reaction under consideration conforms to the model by assuming that $n = 1$ and calculating E at different temperatures throughout the curve, using Eqn. (12).

E. — If, from (*D*), $n \approx 1$ and T_m lies within the linear region (or E is constant at $n = 1$ and T_m lies within the region of constant E), calculate Z from the expression[1,7]

$$Z = \frac{BE\,e^{E/RT_m}}{RT_m^2} \tag{17}$$

F. — If a series of values for E was not obtained in (*D*), E can now be calculated for various values of x by means of Eqn. (12).

RESULTS AND DICUSSION

A search of the literature and considerable experimental work indicate that there is no such thing as a completely "well behaved" decomposition of a pure liquid or solid. Complete kinetics treatments of such systems are extremely scarce, though the literature is full of results. Many of the results are useful for technical purposes, making an actual prediction of an overall rate possible, and it is important to note that almost without exception first-order dependence of rate on active mass is assumed to obtain the practical results.

One careful study of a system of the type of interest here is contained in Robertson's work[8] on the explosive RDX (hexahydro-1,3,5-trinitro-*s*-triazine). Robertson assumed first-order kinetics to obtain his kinetics constants. We have used his results to compute critical temperatures for the explosive according to the method of Zinn and Mader[9]; the computed results were in excellent agreement with experimental values determined in several different geometries.

The results presented in Table I show that the RDX decomposition is less complex than that of the closely related explosive HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). Fig. 1 shows a representative DSC curve for RDX, and Fig 2 shows the data obtained from the curve plotted in the form specified by Eqn. (13). The points can be seen to lie on a straight line between 7.4 and 80% decomposition, and n is found to be 1.3. The thermal decomposition of RDX thus complies reasonably well with the requirements of the assumed model.

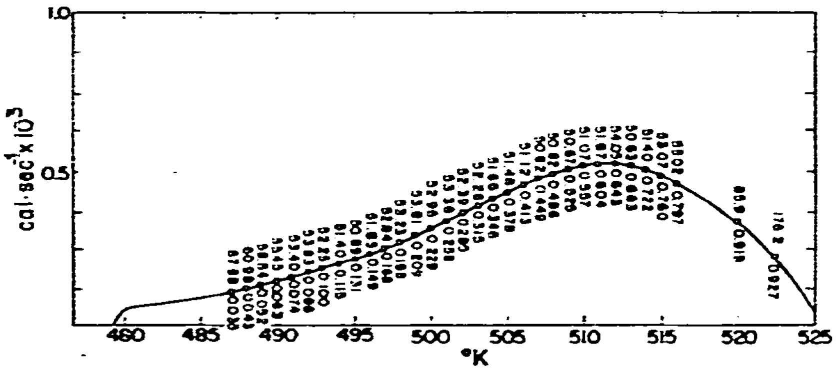

Fig. 1. DSC decomposition curve for RDX. Sample weight, 0.000978 g; DSC range, 8 mcal full-scale; x = 12,053.6 mm·sec; B = 0.1667 °K·sec^{-1}; T_m = 512 °K. Numbers inside the curve refer to fraction decomposed, x; numbers outside the curve refer to the activation energy as calculated according to Eqn. (12). A constant n = 1.3 is assumed.

Without a primary standard condensed-phase reaction it is impossible to determine the accuracy of any method for the determination of kinetics constants; however, the various methods can be compared, and in Table II we have summarized the results obtained by analyzing the DSC curve for RDX in several different ways.

The simplified method of Rogers and Morris[5] for the determination of activation energies from a DSC curve does not require a sample weight or heat of reaction.

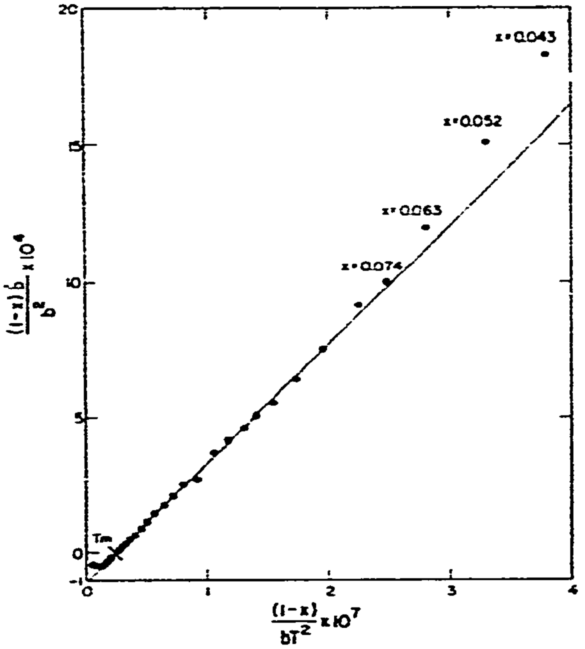

Fig. 2. Plot of RDX decomposition data (x, T, slope, and deflection) from DSC curve shown in Fig. 1 according to Eqn. (13).

TABLE II

COMPARISON OF APPARENT ACTIVATION ENERGIES OF RDX DETERMINED BY DIFFERENT METHODS

Method	*E* (*kcal·mole*$^{-1}$)	*log Z* (*Z in sec*$^{-1}$)
Robertson[8], $n = 1$[a]	47.5	18.5
Rogers and Morris[5], $n = 0$[a]	48.4	18.4
Kissinger method[1]	28.6	10.6
Least-squares fit of rate constants		
from Eqn. 8, $n = 1$[a]	50.6	19.6
Eqn. 10, all data, $n = 0.78$[b],	50.3	19.7
10–80% decomposed, $n = 0.9$[b]	50.0	
Eqn. 12, average between 10 and 80%		
decomposed, $n = 1$[a]	48.2	18.8
$n = 1.3$[b]	52.1	20.6
Eqn. 13, all data, $n = 1.36$[b]	53.0	20.8
10–80% decomposed, $n = 1.3$[b]	52.0	20.4
Eqn. 14, average of multiple determinations,		
$n = 1$[a]	50.8	19.9

[a] Order assumed.
[b] Order determined.

However, the method does require that $(1-x)^n \cong 1$ so that b can be substituted for k. This requires either $n = 0$, which is inconsistent with Eqn. (3), or $x \cong 0$. Thus the method can yield a good approximation only when x is small. Nonetheless, the

Rogers and Morris result, obtained from early data points only, agrees quite well with Robertson's values and with the results obtained from Eqn. (12) with n assumed equal to 1. Also shown in Table II are results obtained by a regression analysis on Eqn. (10), using values of x obtained from Eqn. (9); this procedure also provides simultaneous "best values" for E, Z, and n, but the computations are more complex than those required by Eqn. (13), and the method does not provide a ready basis for determining over what range of values (if any) the reaction conforms to the model.

Finally, we note that all the DSC methods are reasonably consistent when compared at the same reaction order.

Fig. 1. illustrates how changes in activation energy during the progress of a reaction can be followed by use of Eqn. (12). Recognizing the fact that in a complex reaction these will be "procedural" activation energies, it is believed that such a treatment makes it possible to separate the components of a complex process. Laidler[10] discussed a method that can be used with isothermal studies to detect autocatalysis or inhibition in a complex reaction. The method is quite laborious, involving the determination of both an apparent (time-based) order and a true (concentration-based) order. Autocatalysis or inhibition can be detected very easily by use of the proposed method. Since the usually observed effect of a catalyst is to decrease E, while an inhibitor causes an increase in the observed E, repeated measurements of E throughout a decomposition allow one easily to detect these phenomena. The RDX decomposition shows signs of both autocatalysis and inhibition.

Some reactions are quite obviously inhibited by products. An example of one that has been studied[11,12] is the silver carbonate decomposition. As the decomposition proceeds, the concentration of CO_2 can build up around the decomposing solid, retarding the decomposition. Aside from the effect of CO_2, it has been noted[12] that a different rate-determining step becomes important after approximately 10% decomposition. The usefulness of being able to determine a series of activation energies at low degrees of conversion is illustrated in Table III. Reported activation energies are 22.8–23.4 kcal·mole^{-1} (ref. 11) and 20 kcal·mole^{-1} (ref. 12), in excellent agreement with the early values determined from the DSC curve. The DSC values extrapolate to a value somewhat less than 20 kcal·mol^{-1} at $x = 0$. Inhibition is clearly shown by the increase in E with x.

TABLE III

DATA FROM DECOMPOSITION OF Ag_2CO_3
SAMPLE WEIGHT, 0.006886 g; $B = 0.1667\,^{\circ}K \cdot sec^{-1}$

T (°K)	x_t	E (kcal·mole^{-1})
450	0.079	22.2
452.5	0.102	24.6
455	0.12[illegible]	28.6
457.5	0.158	69.6
460	0.198	115.5
462.5	0.272	151.9

The degree of precision that can be attained with Eqn. (12) is shown by the data in Fig. 1. The 25 values between 491 and 515 °K give a mean activation energy of 52.1 kcal·mole^{-1} with a standard deviation of 1.1 kcal·mole^{-1} (2.1 %).

Of the five different thermochemical methods discussed (Table II), the proposed method [Eqns. (12)–(14)] appears to give the most information without sacrifice in accuracy potential. It provides a method of establishing the degree of complexity of the reaction in question to tell whether any method could give a true activation energy, and at the same time makes it possible to determine the activation energy, all from a single DSC curve.

A clever isothermal gasometric method, involving the direct determination of the differential rate, has been presented by Keenan and Dimitriades[13]. They show the advantages of a differential method; however, as in most methods involving measurement of products, a mechanism had to be assumed and corrections for volatility had to be made. When the reacting system must be quenched for the measurement of x, the extent of reaction during heatup and quench cycles must be considered. The care with which corrections are made may largely determine the accuracy of manometric or gasometric methods.

None of the methods for studying overall reaction rates, whether manometric, gasometric, gravimetric, or thermochemical, will give a true activation energy for a complex reaction. The proposed thermochemical method makes it possible to detect and to study complexity.

It is believed that the more rigorous of the DSC methods have at least the accuracy potential of the other methods for studying overall reaction rates, and the methods certainly have distinct advantages in sample size, speed, and ease of operation.

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