

EVALUATION OF THE NON-ISOTHERMAL RATE EQUATION PROPOSED BY ŠESTÁK AND BERGGREN BY COMPUTER METHODS

THE DEHYDRATION OF MANGANESE(II) FORMATE DIHYDRATE

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ABSTRACT

The equation

$$\frac{d\alpha}{dt} = k\alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p$$

proposed by Šesták and Berggren was applied to the dehydration of $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ as studied by differential scanning calorimetry. Systematic variation of the parameters m , n , and p and linear least-squares analysis of the Arrhenius plot resulting from each equation were accomplished with a computer program. The method was found to be successful for preliminary appraisal of reaction mechanism or as a means of checking isothermal results. The problem of finding a suitable fraction of reaction, α , over which any particular rate law is valid, is somewhat circumvented by the ease with which multiple runs may be made with various α ranges. The possible rate expressions found for $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ using the Šesták–Berggren equation include those reported in the literature for $0.15 \leq \alpha \leq 0.45$, and activation energies for interfacial advance agree with those obtained in previous studies.

INTRODUCTION

Non-isothermal thermoanalytical procedures for evaluating kinetic parameters are exceedingly convenient because only small samples are required and the method is rapid. Moreover, the technique circumvents one problem encountered in isothermal studies, namely, reaction while the sample is brought to the desired temperature. Nevertheless, non-isothermal procedures are not without limitations which can lead to misinterpretations of results^{1–3}. For solid-phase transformations these can often be traced to the fact that the reactions must usually be described in terms of at least three stages—induction, growth, and decay—each of which can involve its own rate law^{4–6}.

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In developing equations for non-isothermal kinetic studies it has been common to assume a rate law of the form

$$\frac{dx}{dt} = k(1-x)^n \quad (1)$$

where x is the fraction of reaction, k is the isothermal rate constant, and n is the order of the reaction⁷⁻¹⁰. While such a rate law is characteristic of homogeneous reactions, it is applicable only in limited circumstances to solid-phase reactions^{3-6,11}. Thus, when non-isothermal procedures are used with solids, a different expression for dx/dt is frequently necessary.

Recently Šesták and Berggren³ summarized the rate laws found most commonly for solid-phase reactions. This led them to propose the following general rate law for solids

$$\frac{dx}{dt} = kx^m(1-x)^n[-\ln(1-x)]^p \quad (2)$$

where m , n , and p are temperature independent constants.

We have tested the utility of this equation for non-isothermal kinetic studies by applying it to the dehydration of manganese(II) formate dihydrate, $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$, which was studied by differential scanning calorimetry. This reaction was chosen because it has been carefully studied by several workers using a variety of methods, and the kinetic processes have been well characterized^{1,11-14}.

EXPERIMENTAL

The $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ was obtained from K & K Laboratories and was recrystallized from hot water. The compound was analyzed for water content by measuring mass loss accompanying thermogravimetry using equipment described elsewhere^{2,5}.

Differential scanning calorimetry

A Perkin-Elmer Differential Scanning Calorimeter (DSC-1B) was used to measure enthalpy changes. Samples which weighed 5-7 mg and which had passed through a 100-mesh sieve were mounted in aluminum pans either without covers or with perforated aluminum covers with a N_2 flow of *ca.* 23 ml min^{-1} . The instrument was calibrated with indium and heating rates of 5 or 10° min^{-1} were employed.

Computational procedure

The general relation between dx/dt and dH/dt , the change of enthalpy with time, given by Thomas and Clarke¹ is

$$\frac{dx}{dt} = \frac{1}{A} \left(\frac{dH}{dt} \right) \quad (3)$$

Combining this equation with eqn (2) gives

$$k = \frac{1}{A} \left(\frac{dH}{dt} \right) x^{-m} (1-x)^{-n} [-\ln(1-x)]^{-p} \quad (4)$$

where A is the total area of the peak. The rate constant, k , was evaluated for the values of m , n and p specified in Table 1. These parameters were incremented at intervals of 0.1 with appropriate intermittent values of $I + \frac{1}{2}$, $I + \frac{1}{3}$, $I + \frac{2}{3}$, and $I + \frac{3}{4}$

TABLE 1
VALUES OF m , n , AND p USED TO EVALUATE EQUATION (4)

m	n	p
0	-4→4	0
0	0, $\frac{1}{2}$	1
0	-1	-11→9 ^a
-4→4	0	0
-4→4	-4→4	0

^a p was varied as $[(1/v) - 1]$ where $-4 \leq v \leq 4$.

where $I = 0, \pm 1, \pm 2, \pm 3$. This method of variation included all of the general and most of the specific equations discussed by Šesták and Berggren. The equations considered by these workers are of greatest interest since they are the ones which have been found to be experimentally or theoretically justified for describing the reactions of solids. These specific equations, when written in the general form of eqns (2) or (4), have the values of m , n , and p tabulated in Table 2.

TABLE 2
VALUES OF m , n , AND p FOR SPECIFIC CASES CONSIDERED BY ŠESTÁK AND BERGGREN

m	n	p	Equation ^a	m	n	p	Equation ^a
0	0	0	(14)	0	1	-0.59, -\frac{1}{2} → -\frac{1}{3}	(23)
0	$\frac{1}{2}$	0	(15)	1	0	0	(24)
0	$\frac{2}{3}$	0	(16)	1	1	0	(25)
<1	0	0	(17)	>1	<1	0	(26)
$\frac{1}{2}$ →1	0.556→0.774	0	(18)	-1	0	0	(27)
0	~ $\frac{1}{2}$	0	(19)	0	0	-1	(28)
0	1	$\frac{1}{2}$	(20)	0	$\frac{1}{2}$	-1	(29)
0	1	$\frac{2}{3}$	(21)	0	0	-1	(30)
0	1	0	(22)				

^a The number in parentheses is the number given to each differential equation in ref. 3.

An XDS Sigma 7 computer was used for all calculations. The program, written in Fortran IV, performs area integrations by Simpson's rule and linear least-squares analysis of the Arrhenius plot for each rate equation. Values of α are calculated using the relation $\alpha = a/A$, where a is the DSC peak area up to the temperature in question and A is the total peak area. Depending on command, the program outputs the total enthalpy change for the reaction, ΔH , rate constants, activation energies, and scatter* about the least-squares regression line over any specified range of α .

In evaluating the results of this study, most consideration was given to those rate equations for which $E_a \geq \Delta H$ (within estimated uncertainties) and for which the scatter was about 0.015 or less or where minima occurred in the scatter as m , n , and p were varied. The limit of 0.015 is arbitrary and was selected due to past experience with graphical displays of data. The average enthalpy change for dehydration of $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ was found to be 13.1 ± 1.0 kcal/mole of H_2O for seven determinations, which agrees with the value of 13.8 ± 0.4 found by solution calorimetry¹². Therefore, only rate expressions for which $E_a \geq 12$ kcal mol⁻¹ were considered¹⁶.

RESULTS AND DISCUSSION

Summary of previous studies on $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$

The dehydration of $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ has been found to be governed by the rate of interfacial advance¹²⁻¹⁴. Moreover, this rate is anisotropic, proceeding more rapidly on the {011} faces of the approximately parallelepiped-shaped crystals than normal to these faces^{12,13}. Eckhardt and Flanagan¹² therefore described the reaction in terms of a contracting-parallelogram rate law:

$$\alpha = \frac{L_1 L_2 - (L_1 - 2k\tau \cos \theta)(L_2 - 2k\tau)}{L_1 L_2} \quad (5)$$

where L_1 and L_2 are crystal dimensions, θ is an angle characteristic of the parallelogram, and $\tau = t - t_0$ where t is the experimental time and t_0 is the time required to establish the complete interface. Subsequent investigations concur with this description^{1,11,13,14}.

Over the range of approximately $0.15 \leq \alpha \leq 0.45$, the dehydration of $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ has been found to obey a linear rate law, $\alpha = k't$. It has been shown that this simple expression yields the same activation energy as eqn (5)^{12,14} and has therefore been used to advantage, particularly in kinetic studies of powdered samples.

*Scatter is defined as the standard error of estimate of Y on X for a line composed of N points and is given by:

$$S_{Y \cdot X} = \sqrt{\frac{\sum Y^2 - a_0 \sum Y - a_1 \sum (XY)}{N}}$$

$$\text{where } a_0 = \frac{\sum Y - a_1 \sum X}{N} \text{ and } a_1 = \frac{N \sum (XY) - (\sum X)(\sum Y)}{N \sum X^2 - (\sum X)^2}$$

For the single crystals of $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ studied by Clarke and Thomas, $L_1 \simeq L_2$ and $\theta = 15.6^\circ$ ¹³. These values make possible another approximation to eqn (5). When $L_1 = L_2$ and $\cos \theta = 1$ ($\cos 15.6^\circ = 0.963$), it reduces to the familiar contracting-square rate law:

$$(1-\alpha)^{\frac{1}{2}} = 1 - k''\tau \quad (6)$$

where $k'' = 2k/L_1$. Although previous workers have not discussed this rate law, it would be expected to yield an activation energy nearly the same as that for eqn (5). It should be noted that the similar contracting-cube (or contracting-sphere, as it is also called) rate law, $(1-\alpha)^{\frac{1}{3}} = 1 - k'''t$, was found to give good data-fit over a wider range of α for the dehydration curves (α versus t) than did eqn (5), but was rejected in view of the anisotropic nature of the reaction¹².

The dehydration of $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ exhibits an activation energy for interfacial advance of 17 ± 1 kcal mol⁻¹ as obtained by a number of different techniques including microscopy^{1, 12-14}.

Application of the Šesták-Berggren equation

The computer program was run with various α ranges for each sample heated in an open pan. No equation was found to describe the reaction satisfactorily for the full range, $0 \leq \alpha \leq 1$. This is not surprising when one considers the possible stages of reaction discussed above. The ranges 0.15-0.45, 0.2-0.7, and 0.0-0.7 were also considered. The first was chosen because previous workers concentrated on this range; the second because past experience had shown it to be useful and to generally encompass the growth stage; and the last for comparative purposes. The results for these ranges are summarized in Table 3 and correspond to rate equations for which $E_a \geq 12$ kcal mol⁻¹ and scatter ≤ 0.015 .

TABLE 3
VALUES OF m , n , AND p WHICH LEAD TO GOOD FITS OF THE
ARRHENIUS PLOTS

Range of α	m	n	p	E_a (kcal mol ⁻¹)
0.0-0.7	0	1	0	24.5
	0	1	$-\frac{2}{3} \rightarrow \frac{1}{2}$	42.0 → 12.1
	$-1 \rightarrow \frac{1}{3}$	$\frac{3}{4} \rightarrow \frac{3}{2}$	0	51.0 → 15.3
0.2-0.7	0	$\frac{1}{2} \rightarrow \frac{11}{10}$	0	18.1 → 25.9
	0	1	$-4 \rightarrow \frac{1}{2}$	128.2 → 12.5
	$-4 \rightarrow \frac{1}{2}$	$2 \rightarrow \frac{3}{4}$	0	118.3 → 12.1
0.15-0.45	0	$-\frac{1}{10} \rightarrow \frac{7}{4}$	0	14.3 → 29.8
	0	1	$-9 \rightarrow \frac{9}{19}$	257.9 → 12.1
	$-4 \rightarrow \frac{1}{2}$	$4 \rightarrow 0$	0	128.7 → 12.1

It can be seen that a wide range of equations and corresponding activation energies can be obtained if one chooses data-fit alone as the criterion of mechanism. The possible rate equations can be further limited by considering those cases which have a relatively small range of m , n , and/or p , and/or yield a limited range of activation energies as the range of α is varied. Thus it appears that the rate equation is of the form:

$$k = \frac{1}{A} \left(\frac{dH}{dt} \right) (1-\alpha)^{-n} \quad (7)$$

where $-1/10 \leq n \leq 7/4$. This includes those experimentally or theoretically justified equations discussed earlier. The activation energies obtained for these rate laws are summarized in Table 4.

TABLE 4
ACTIVATION ENERGIES OBTAINED FOR KNOWN RATE EQUATIONS

m	n	p	E_a (kcal mol ⁻¹) ^a			Equation
			$0.0 \leq \alpha \leq 0.7$	$0.2 \leq \alpha \leq 0.7$	$0.15 \leq \alpha \leq 0.45$	
0	0	0	17.3 ± 0.1	11.4 ± 0.3	15.8 ± 0.3	linear
0	1/2	0	21.1 ± 0.1	18.2 ± 0.1	19.8 ± 0.3	contracting-square
0	2/3	0	22.4 ± 0.2	20.5 ± 0.2	21.2 ± 0.4	contracting-cube
0	1	0	24.8 ± 0.3	25.1 ± 0.5	23.9 ± 0.4	unimolecular

^a Error limits are average deviations from the mean.

Had the data been reduced using eqn (1) as it is commonly applied, the reaction might be described by a reaction order ranging from 0 to 1.5. This gives activation energies ranging from 15.1 to 29.0 kcal mol⁻¹ for $0.15 \leq \alpha \leq 0.45$. The best data-fit for this expression occurred at $n = 0.8$, yielding an activation energy of 22.0 ± 0.1 kcal mol⁻¹.

As previously stated, the linear rate law has been employed in previous work to describe the dehydration of $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ over the range $0.15 \leq \alpha \leq 0.45$; furthermore, the contracting-square rate law should likewise describe the system, possibly over an even larger α range. The activation energies obtained for these rate laws, 15.8 ± 0.3 and 18.2 ± 0.1 kcal mol⁻¹, respectively, are in good agreement with the literature value of 17 ± 1 kcal mol⁻¹.

It should be pointed out that isothermal studies are generally interpreted in terms of the integrated forms of the various rate laws considered by Šesták and Berggren. Where the integrated expression contains time raised to a power, q , the rate constant, K , is not directly proportional to the rate constant, k , obtained from eqn (2). In fact, $k = qK^{1/q}$, so that the activation energies obtained using that equation will differ from those obtained using the integrated rate law by a factor of $1/q$.

Finally, samples which were heated in covered pans gave activation energies on the order of three times greater than those above for comparable equations and α ranges. This is probably the result of the ready rehydration of the compound. As has been found previously, water vapor pressures have a considerable effect on the kinetics of dehydration^{1,2}.

CONCLUSIONS

As applied here, eqn (2) appears useful for preliminary appraisal of reaction mechanisms as proposed by Šesták and Berggren³. In particular, the agreement of activation energies together with minima in scatter support the utility of the equation. Moreover, the present non-isothermal procedure can provide a rapid check of results obtained by isothermal methods. In many instances it may not be possible to conduct the diffraction, microscopy, or other studies necessary to determine the true reaction mechanism (owing, for example, to the lack of suitable crystals). In such cases, especially where a homologous series of compounds is studied for trends in kinetic parameters, use of eqn (2) appears to be more informative than use of eqn (1). The results underscore the fact that the deduction of a specific mechanism from satisfactory data-fit alone is a highly questionable procedure.

One problem in the use of the Šesták–Berggren equation, or for that matter, any rate expression is choice of a suitable range of α , as Tables 3 and 4 indicate. It therefore appears advisable to evaluate the data over several regions. Care must be taken when using sample pan covers to determine whether this has any effect on kinetic results.

The particular advantages of using the computer program to evaluate eqn (2) include the capability of rapid, systematic variation of the parameters m , n , and p , allowing one to observe trends in activation energies and minima in scatter. Also, the changing of α ranges is easily accomplished and its effect is readily apparent.

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Low scatter may result from symmetric distribution of experimental points about the regression line. The computer program has been modified to include a *t*-test which indicates the degree of linearity. Use of this additional statistical test does not appreciably change the reported results.