

SENSITIVITY OF THE MECHANISM DETERMINED BY ISOTHERMAL METHODS TO ERRORS IN α

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ABSTRACT

The effects of errors in α on the mechanism of a solid state reaction giving the best fit to isothermal (α , t) data were investigated. Errors were introduced into part or all of each data set for first-order and A2 processes. In general, the errors required to produce a change in the indicated rate law were similar in magnitude to those required to produce a change in mechanism by the Reich and Stivala procedure for nonisothermal data. In some cases, errors in α as small as +0.010 can result in a different rate law giving a better fit to the data.

INTRODUCTION

It is a common idea that isothermal methods are preferable to nonisothermal ones for kinetic studies on solid state reactions [1]. Reich and Stivala have described a useful method based on data obtained from nonisothermal studies at different heating rates [2]. That method makes use of 12 commonly encountered rate laws that cover a wide variety of solid state processes. Prior to the availability of that method, the usual nonisothermal methods were based on the rate law

$$\frac{d\alpha}{dt} = \frac{A}{\beta} (1 - \alpha)^n e^{-E/RT} \quad (1)$$

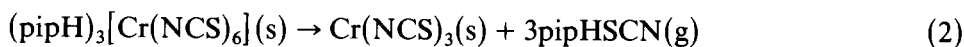
where the symbols have their usual meanings [3–8]. However, isothermal methods can easily test a large number of rate laws. As the determination of α from any TG experiment is subject to some error, it is of considerable importance to determine the effects that errors in α have on the mechanism indicated. We have recently completed such a study which indicates that the Reich and Stivala procedure reliably indicates the correct mechanism in some cases even though relatively large errors in α are present. In other cases, small errors can cause a change in the indicated mechanism [9]. While the question of the effects that errors in α have on the mechanism indicated by the Reich and Stivala procedure has been answered, uncertainty remains as to the effects that such errors have on the mechanism indicated from

isothermal data. We have examined this problem and this report presents the results of that work.

METHODS

In isothermal kinetic studies, α is determined as a function of time, and the data are fitted to rate laws representing a variety of mechanisms. In this work, 17 different rate laws were employed using a least-squares routine. These rate laws are those normally encountered for solid state reactions [10].

The (α, t) data sets from several sources were altered by introducing errors in α . Both experimental and calculated (α, t) data were used. The reaction



(where pip \equiv piperidine) has been found to obey a first-order, F1: $-\ln(1 - \alpha)$, rate law [11]. Experimental data for this reaction carried out at 235 °C were used as one data set. Calculated data sets were generated using a first-order rate law with $k = 0.015 \text{ min}^{-1}$ and an Avrami A2: $[-\ln(1 - \alpha)]^{1/2}$ rate law, also with $k = 0.015 \text{ min}^{-1}$.

Errors in α were introduced into each of these data sets using several patterns. These altered data sets were then analyzed according to 17 rate laws using a computer program written in BASIC.

RESULTS AND DISCUSSION

In TG experiments, errors in α could occur in a variety of ways. In some runs, all the values of α might be slightly low or high for some systematic reason. Errors might also be more random with some of the values being high and others being low. Consequently, the errors introduced into the α values were introduced in several ways. These include adding or subtracting an increment to all the α values, adding increments to half the α values while subtracting increments from the others, etc. These patterns were followed to simulate most of the types of errors that could be expected to be encountered in TG experiments.

To determine how much error in α is required to change the indicated rate law, the calculated data set for the first-order rate law was altered by adding increments of 0.010 to each α value until the rate law changed. The results of this type of calculation are shown in Table 1. The change in rate law occurred at an error of 0.040 and with that amount of error the best fitting rate law was the two-dimensional diffusion control, D2: $(1 - \alpha)\ln(1 - \alpha) + \alpha$. Subtracting increments from each α also led to this being the best

TABLE 1

Effects of errors in α on the rate law obtained from calculated (α, t) data fitting a first-order rate law

Time (min)	α	Error in α ^a						
		+0.040	-0.100	+0.010	-0.030	+0.040	+0.030	-0.020
20	0.25918	+0.040	-0.100	+0.010	-0.030	+0.040	+0.030	-0.020
40	0.45119	+0.040	-0.100	+0.010	-0.030	-0.040	-0.060	-0.020
60	0.59343	+0.040	-0.100	+0.010	-0.030	+0.040	+0.030	-0.020
80	0.69880	+0.040	-0.100	-0.010	+0.030	-0.040	-0.060	+0.040
100	0.77687	+0.040	-0.100	-0.010	+0.030	+0.040	+0.030	+0.040
120	0.83470	+0.040	-0.100	-0.010	+0.030	-0.040	-0.060	+0.040
Best rate law ^b	F1	D2	D2	D2	A1.5	D1	D1	A1.5
Corr. coeff.	1.00000	0.99953	0.99880	0.99971	0.99769	0.96420	0.95620	0.99803
Second-best rate law ^b	D2	F1	F1	F1	R3	R3	R2	R3
Corr. coeff.	0.99942	0.99951	0.99880	0.99953	0.99730	0.96384	0.95599	0.99751

^a Error in α necessary to produce a change in the indicated rate law.^b The rate laws are as follows: F1, $-\ln(1-\alpha)$; D2, $(1-\alpha)\ln(1-\alpha)+\alpha$; A1.5, $[-\ln(1-\alpha)]^{2/3}$; R3, $1-(1-\alpha)^{1/3}$; R2, $1-(1-\alpha)^{1/2}$; and D1, α^2 .

fitting rate law when the error reached -0.100 . Errors were also introduced by adding increments to α in the first half of the data set and subtracting increments in the last half. These procedures were used to simulate the systematic and random errors that might occur during TG experiments. In this way, a combination of errors of $+0.010$ and -0.010 led to the D2 mechanism being the best fitting rate law. Errors of this magnitude could well arise because of variations between TG runs. In each of these cases, the first-order rate law appears as the second-best fitting one.

Table 1 also shows the effects of introducing subtractive errors in the first half of the data set and additive errors in the last half. In this way, errors of -0.030 and $+0.030$ cause the data to give a best fit with the A1.5: $[-\ln(1-\alpha)]^{2/3}$ mechanism with the R3: $1-(1-\alpha)^{1/3}$ giving the second best fit. The results obtained using other combinations of additive and subtractive errors within the same data set are also shown in Table 1. In most of these cases, the correlation coefficients are at least 0.998 so that a good fit of the data is sometimes provided by an incorrect rate law.

To determine how experimental (α, t) data respond to errors in α , data for the decomposition of $(\text{pipH})_3[\text{Cr}(\text{NCS})_6]$ at 235°C were used. These data and the effects of various types of errors in α are shown in Table 2. When errors are added to all the α values, the rate law changes from first-order to R3 when the error is $+0.090$. The first-order law provides the second-best fit in that case. Subtractive errors as large as -0.100 to all the α values did not change the rate law from F1. Table 2 also shows the effects of introducing additive errors to the first half of the data set and subtractive

TABLE 2

Effects of errors in α on the rate law obtained for experimental (α , t) data fitting a first-order rate law

Time (min)	α	Error in α ^a						
		+0.090	-0.100	+0.020	-0.100	+0.030	+0.020	-0.050
10	0.117	+0.090	-0.100	+0.020	-0.100	+0.030	+0.020	-0.050
20	0.244	+0.090	-0.100	+0.020	-0.100	-0.030	-0.040	-0.050
24	0.288	+0.090	-0.100	+0.020	-0.100	+0.030	+0.020	-0.050
30	0.347	+0.090	-0.100	+0.020	-0.100	-0.030	-0.040	-0.050
40	0.434	+0.090	-0.100	+0.020	-0.100	+0.030	+0.020	-0.050
50	0.515	+0.090	-0.100	-0.020	+0.100	-0.030	-0.040	+0.100
60	0.585	+0.090	-0.100	-0.020	+0.100	+0.030	+0.020	+0.100
70	0.644	+0.090	-0.100	-0.020	+0.100	-0.030	-0.040	+0.100
80	0.696	+0.090	-0.100	-0.020	+0.100	+0.030	+0.020	+0.100
90	0.731	+0.090	-0.100	-0.020	+0.100	-0.030	-0.040	+0.100
Best rate law ^b								
Corr. coeff.	F1	R3	F1	D1	F1	R3	R3	A1.5
	0.99983	0.99939	0.99936	0.99897	0.98910	0.98264	0.98261	0.99242
Second-best rate law ^b								
Corr. coeff.	D1	F1	R3	F1	A1.5	F1	F1	F1
	0.99841	0.99924	0.99713	0.99879	0.98905	0.98221	0.98233	0.99234

^a Error in α necessary to produce a change in the indicated rate law.^b The rate laws are as follows: F1, $-\ln(1 - \alpha)$; R3, $1 - (1 - \alpha)^{1/3}$; D1, α^2 ; and A1.5 $[-\ln(1 - \alpha)]^{2/3}$.

errors to the second half. In this way, the best fitting rate law changes from F1 to D1: α^2 when the errors are +0.020 and -0.020. When subtractive errors are used in the first half and additive errors are introduced into the second half of the data set, errors of -0.100 and +0.100 still result in F1 providing the best fit. In this case, the correlation coefficient is only 0.9891, however.

Introducing errors of alternating sign into alternate α values leads to R3 giving the best fit when the errors are +0.030 and -0.030, respectively. Table 2 also shows the effects of introducing errors in other patterns. It is obvious that in some cases errors within the range of normal experimental errors can cause a change in the indicated rate law.

Having investigated the behavior of first-order processes toward errors in α , it remained to determine the sensitivity of data for some other rate laws toward these errors. Accordingly, a data set of (α , t) values was constructed for the A2: $[-\ln(1 - \alpha)]^{1/2}$ rate law. These data and the effects of errors of several types in α are shown in Table 3. It can be seen that an additive error of +0.030 to all the α values causes the best fit to be provided by the A3: $[-\ln(1 - \alpha)]^{1/3}$ rate law with the A2 rate law giving the second-best fit. Subtractive errors of -0.030 result in the best fitting rate law being A1.5 with A2 giving the second-best fit. An error of +0.040 in the first half of the data set and an error of -0.040 in the second half results in the best fitting

TABLE 3

Effects of errors in α on the rate law obtained for calculated (α , t) data fitting an A2 rate law

Time (min)	α	Error in α ^a						
		+0.030	-0.030	+0.040	-0.062	+0.060	+0.045	-0.030
17	0.06296	+0.030	-0.030	+0.040	-0.062	+0.060	+0.045	-0.030
33	0.21732	+0.030	-0.030	+0.040	-0.062	-0.060	-0.090	-0.030
49	0.41738	+0.030	-0.030	+0.040	-0.062	+0.060	+0.045	-0.030
66	0.62473	+0.030	-0.030	-0.040	+0.062	-0.060	-0.090	+0.060
83	0.78776	+0.030	-0.030	-0.040	+0.062	+0.060	+0.045	+0.060
100	0.98460	+0.030	-0.030	-0.040	+0.062	-0.060	-0.090	+0.060
Best rate law ^b								
Corr. coeff.	A2	A3	A1.5	R1.5	A2	A3	F2	A3
	1.00000	0.99939	0.99916	0.99894	0.99884	0.96820	0.96180	0.99829
Second-best rate law ^b								
Corr. coeff.	R1.5	A2	A2	A2	R1.5	F2	B1	A2
	0.99841	0.99909	0.99910	0.99871	0.99327	0.96819	0.96180	0.99818

^a Error in α necessary to produce a change in the indicated rate law.^b The rate laws are as follows: A2, $[-\ln(1-\alpha)]^{1/2}$; A3, $[-\ln(1-\alpha)]^{1/3}$; R1.5, $1-(1-\alpha)^{2/3}$; A1.5, $[-(\ln(1-\alpha))^{2/3}]$; F2, $1/(1-\alpha)$; and B1, $\ln[\alpha/(1-\alpha)]$.

rate law being $1-(1-\alpha)^{2/3}$. The results of introducing errors in other patterns are also shown in Table 3.

The results shown in Tables 1–3 indicate that the rate law indicated from isothermal TG studies is rather sensitive to certain types of errors, but rather insensitive to other types of errors. In general, the magnitudes of the errors in α needed to change the rate law are similar to those that result in a change in rate law from nonisothermal studies [9]. If the errors occur in certain patterns, inaccuracies in α as small as +0.010 and -0.010 can result in a different rate law providing a better fit to the data. It appears from the limited number of possibilities used here that the F1 case is somewhat more sensitive to errors in α than is the A2 case. This was also shown [9] for the Reich and Stivala procedure. It is likely that data fitting other rate laws would behave similarly with errors in α .

From the results obtained in this work and those presented earlier for data from nonisothermal experiments [9] using the procedure of Reich and Stivala, it appears that there is no great difference between isothermal and nonisothermal methods with respect to sensitivity to errors in α . We have, however, found the reproducibility of isothermal TG runs to be somewhat better for the decomposition of $(\text{pipH})_3[\text{Cr}(\text{NCS})_6]$ and the dehydration of $\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ [11]. When TG is the basis for the kinetic analysis, it appears that there is little difference between isothermal and nonisothermal methods for determining the mechanisms of solid state reactions. Given the magnitudes of the experimental errors present in α , it is imperative that

neither method be used to assign a mechanism on the basis of a limited number of experiments.

REFERENCES

- 1 A.R. West, *Solid State Chemistry and Its Applications*, Wiley, New York, 1984, p. 113.
- 2 L. Reich and S.S. Stivala, *Thermochim. Acta*, 62 (1983) 129.
- 3 A.W. Coats and J.P. Redfern, *Nature (London)*, 201 (1964) 68.
- 4 L. Reich and S.S. Stivala, *Thermochim. Acta*, 36 (1980) 103.
- 5 J.H. Horowitz and G. Metzger, *Anal. Chem.*, 35 (1964) 1464.
- 6 J.R. MacCallum and J. Tanner, *Nature (London)*, 225 (1970) 1127.
- 7 J.E. House, Jr., and J.D. House, *Thermochim. Acta*, 61 (1983) 277.
- 8 J.E. House, Jr., and D.K. Tcheng, *Thermochim. Acta*, 64 (1983) 195.
- 9 J.E. House, Jr., and D.G. Beck, *Thermochim. Acta*, 154 (1989) 225.
- 10 J. Sestak and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.
- 11 J.E. House, Jr., and L.A. Marquardt, unpublished results.