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THE EFFECTS OF ERRORS IN α ON THE MECHANISM INDICATED BY THE REICH AND STIVALA PROCEDURE

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ABSTRACT

The effects of errors in α on the mechanism indicated by the Reich and Stivala procedure were studied. It was found that in some cases substantial errors, larger than those present in normal TG experiments, resulted in no change in the indicated mechanism. However, the method appears to be very sensitive to combinations of errors of certain types and to what the correct mechanism is. In those cases, errors in α as small as 0.005 can result in an incorrect rate law being indicated as the correct one.

INTRODUCTION

There is a general notion that isothermal methods probably yield kinetic information of greater reliability than that obtained by nonisothermal methods [1]. Certainly that is true when procedures for analyzing (α, T) data are based on a rate law of the type

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}(1-\alpha)^n \, \mathrm{e}^{-E/RT} \tag{1}$$

where the symbols have their usual meaning. Numerous procedures are based on this rate law [2–7]. However, solid state reactions are known which may follow numerous other types of rate laws based on nucleation, reaction order, diffusion, power laws, etc. [8]. Only a few of these can be reduced to a form involving $(1-\alpha)^n$ as shown in eqn. (1). Reich and Stivala have developed a powerful procedure based on nonisothermal data from heating rates differing by a factor of two which removes that difficulty [9]. Their procedure tests the fit of 12 different rate laws by computing the standard error of estimate (SEE) for each. However, the procedure is still subject to sample-to-sample variations [10–13]. We have begun an exhaustive comparison of this method with isothermal methods to compare their consistency in indicating a correct rate law. In the work reported here, we have investigated the effects that errors in α have on the rate law indicated by the Reich and Stivala method [9].

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METHODS

The Reich and Stivala procedure requires values of α at various temperatures, obtained at heating rates differing by a factor of two [9]. The α values used in this work were obtained for two reactions

$$K_2[Cu(C_2O_4)_2] \cdot 2H_2O(s) \rightarrow K_2[Cu(C_2O_4)_2](s) + 2H_2O(g) \qquad (2)$$

$$(pipH)_3[Cr(NCS)_6](s) \rightarrow Cr(NCS)_3(s) + 3pipHSCN(g) \qquad (3)$$

where pip = piperidine. These reactions have been the subject of an extensive comparison of isothermal and nonisothermal kinetic methods [14]. For the reaction shown in eqn. (2), the mechanism is the Avrami–Erofeev mechanism with an index of 2, A2: $[-\ln(1-\alpha)]^{1/2}$, while the reaction shown in eqn. (3) follows a first-order, $-\ln(1-\alpha)$, rate law [14]. These reactions were selected so that the effects of errors could be determined for reactions following different rate laws.

For the first reaction, data for runs at 2.5 and 5 °C $\min^{-1}$ were chosen, and for the second reaction, data from runs at 5 and 10 °C $\min^{-1}$ were used. Then, various amounts of error were introduced into the α values by adding or subtracting a specific quantity to each value. This procedure was continued with increasing amount of error until the error was large enough to cause the rate law indicated to change. In some cases, the α values for only one of the heating rates were altered and in other cases errors were introduced into the data from both heating rates. These procedures were followed so that the effects of errors arising in a variety of ways could be evaluated. All calculations were carried out using a microcomputer with the program in BASIC given by Reich and Stivala [9].

RESULTS AND DISCUSSION

To determine how much error in α was necessary to change the A2 rate law indicated for the reaction shown in eqn. (2), increments were added to the α values from the run at 5 °C $\min^{-1}$ while leaving the data from the run at 2.5 °C $\min^{-1}$ unchanged. This procedure was repeated with increasing increments to α until the rate law changed. Table 1 shows the results of this iterative process. It can be seen that no change in the indicated best-fitting rate law occurred until the error added to α reached 0.056. At that point, the rate law indicated as the best-fitting one changed from A2 to A1.5. Up to that amount of error, A2 provided the best fit and A1.5 the second best fit. It can be seen that the SEE increases for fitting the A2 rate law, while that for the fit of the A1.5 rate law decreases as the error added to α is increased. Finally, when the error in α reaches 0.056, the SEE for the A1.5 rate law is smaller than that for the A2 rate law.

TABLE 1

Effects of errors in α on the rate law and SEE for dehydration of $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$

	Point	α	Error in α				
5 °C min^{-1}	1	0.226	+0.050	+0.053	+0.054	+0.055	+0.056
	2	0.303	+0.050	+0.053	+0.054	+0.055	+0.056
	3	0.358	+0.050	+0.053	+0.054	+0.055	+0.056
	4	0.450	+0.050	+0.053	+0.054	+0.055	+0.056
	5	0.520	+0.050	+0.053	+0.054	+0.055	+0.056
	6	0.610	+0.050	+0.053	+0.054	+0.055	+0.056
2.5 °C min^{-1}	1	0.666	0	0	0	0	0
	2	0.764	0	0	0	0	0
	3	0.848	0	0	0	0	0
	4	0.912	0	0	0	0	0
	5	0.953	0	0	0	0	0
	6	0.975	0	0	0	0	0
Best rate law		A2	A2	A2	A2	A2	A1.5
SEE $\times 10^2$		1.27	3.91	4.16	4.25	4.33	4.47
Second-best law		A1.5	A1.5	A1.5	A1.5	A1.5	A2
SEE $\times 10^2$		11.1	5.56	5.26	5.16	5.06	6.76

Permutations of the various ways in which errors in α can be introduced leads to a prohibitively large number of possibilities. In order to simulate the types of errors that could be expected to arise experimentally, calculations were performed in which the errors were introduced in several patterns. In each case, the amount of error introduced was changed systematically until a change in the indicated rate law resulted. Error introduced to α was limited to a maximum of 0.100 in most cases assuming that experimental errors larger than this amount were unlikely. In a few cases, even errors of this magnitude produced no change in the best-fitting rate law. The results of these calculations are shown in Table 2 for the dehydration of $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$.

Several conclusions can be reached by examination of the data shown in Table 2. First, when error is introduced into only the data obtained at 5 °C min^{-1}, the indicated rate law is much more sensitive to added errors than subtracted errors. An added error of only 0.056 causes a change in rate law while a larger subtracted error (-0.124) is required. Also, when the error is an added one, the indicated best rate law changes from A2 to A1.5. When the error is a subtracted one, the best-fitting rate law changes from A2 to P3. However, when the 2.5 °C min^{-1} data set is altered and the 5 °C min^{-1} one is unaltered, the results are quite different. The added error required to change the indicated best-fitting rate law is larger (> 0.100) than that for the subtracted error (-0.070). There is no change in the best-fitting rate law even when an error of $+0.100$ is introduced by addition to the data from the 2.5 °C min^{-1} run.

TABLE 2

Effects of errors in α on the rate law and SEE for the dehydration of $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$

	Point	α	Error in α [a]												
5 °C min^{-1}	1	0.226	−0.124	+0.056	0	0	+0.100	−0.090	−0.100	+0.030	+0.100	+0.050	+0.100	−0.10
	2	0.303	−0.124	+0.056	0	0	+0.100	−0.090	−0.100	+0.030	+0.100	−0.100	−0.050	+0.20
	3	0.358	−0.124	+0.056	0	0	+0.100	−0.090	−0.100	+0.030	+0.100	+0.050	+0.100	−0.10
	4	0.450	−0.124	+0.056	0	0	+0.100	−0.090	−0.100	+0.030	+0.100	−0.100	−0.050	+0.20
	5	0.520	−0.124	+0.056	0	0	+0.100	−0.090	−0.100	+0.030	+0.100	+0.050	+0.100	−0.10
	6	0.610	−0.124	+0.056	0	0	+0.100	−0.090	−0.100	+0.030	+0.100	−0.100	−0.050	+0.20
2.5 °C min^{-1}	1	0.666	0	0	−0.070	+0.100	+0.100	−0.090	+0.100	−0.030	+0.100	+0.050	−0.050	−0.10
	2	0.764	0	0	−0.070	+0.100	+0.100	−0.090	+0.100	−0.030	−0.100	−0.100	+0.100	+0.20
	3	0.848	0	0	−0.070	+0.100	+0.100	−0.090	+0.100	−0.030	+0.100	+0.050	−0.050	−0.10
	4	0.912	0	0	−0.070	+0.100	+0.100	−0.090	+0.100	−0.030	−0.100	−0.100	+0.100	+0.20
	5	0.953	0	0	−0.070	+0.100	+0.100	−0.090	+0.100	−0.030	+0.100	+0.050	−0.050	−0.10
	6	0.975	0	0	−0.070	+0.100	+0.100	−0.090	+0.100	−0.030	−0.100	−0.100	+0.100	+0.20
Best rate law		A2	P3	A1.5	A1.5	A2	A2	P3	A2	A1.5	A2	A2	A2	A2
SEE × 10^2		1.27	18.6	4.47	4.99	10.9	5.40	6.21	19.0	4.90	5.32	4.3	13.8	10.8
Second-best law		A1.5	A2	A2	A2	A1.5	A1.5	A2	P3	A2	A1.5	P3	A1.5	A1.5
SEE × 10^2		11.1	18.7	6.76	6.21	20.8	10.9	6.88	20.9	4.91	12.0	11.2	17.7	16.6

[a] Magnitude of the error required to cause a change in indicated rate law.

When errors are introduced by addition to the α values for both the 2.5 and 5 °C min^{-1} runs, an error as large as 0.100 in the data points for each set produced no change in the best-fitting rate law. The calculation is very tolerant to errors of this type. An error as large as $-$0.090 was required when subtractive errors were introduced to both data sets before the indicated rate law changed (in this case to P3). As expected, for some of the cases where large errors were required to produce a change in indicated rate law, the SEE increased substantially even though the indicated rate law remained unchanged.

The effects of adding errors to one data set while subtracting errors from the other were also investigated. When the subtraction was from the data from the 5 °C min^{-1} run and the addition was to the data from the 2.5 °C min^{-1} run, errors of $-$0.100 and +0.100 could be tolerated without a change in the indicated rate law (although the SEE is rather large, 0.190). Experimental errors of this magnitude are unlikely. When the errors were reversed, 0.030 added to the data from the 5 °C min^{-1} run and 0.030 subtracted from the data from the 2.5 °C min^{-1} run, the best-fitting rate law was changed to A1.5. Experimental errors of this magnitude are entirely possible with the usual TG equipment.

Finally, the effects of introducing errors of alternating signs were examined. This was done by adding or subtracting increments to α in alternate data points. The results shown in Table 2 indicate that errors as large as 0.100 still allow an A2 mechanism to be identified although the SEE is larger than with the unaltered data sets. When the increments in α for alternate data points are of unequal magnitude (+0.050 and $-$0.100), the indicated rate law is still A2, but the second-best-fitting rate law is changed to P3 from A1.5. When the increments were reversed in magnitude (+0.100 and $-$0.050), the best-fitting rate law was still A2 and the second best was A1.5, although the SEE values were large. Even when the increments were $-$0.100 and +0.200, the same best-fitting and second-best-fitting rate laws were indicated (A2 and A1.5).

The decomposition of $(\mathrm{pipH})_3[\mathrm{Cr(NCS)_6}]$, which follows a first-order (F1) rate law [14], was chosen as the second reaction for study to determine the effects of errors in α. Table 3 shows the unaltered data sets and the results of the calculations using data sets altered to include errors in α. The results show that there are significant differences between the effects of errors in this case compared with those for the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ where the A2 rate law provided the best fit.

First, the magnitude of the errors required to change the rate law are much smaller in this case. Adding 0.050 to the α values for the data from the 10 °C min^{-1} run results in the D4 rate law providing the best fit, while the F1 rate law provides the second best fit. Subtracting only 0.010 from each α for the 10 °C min^{-1} run while leaving those for the 5 °C min^{-1} run unchanged results in the best-fitting rate law being R3. When the alterations

TABLE 3

Effects of several types of errors in α on the rate law and SEE for decomposition of $(pipH)_3[Cr(NCS)_6]$

	Point	α	Error in α [a]										
10 °C min^{-1}	1	0.229	−0.010	+0.050	0	0	+0.100	−0.060	−0.005	+0.030	+0.120	+0.100
	2	0.303	−0.010	+0.050	0	0	+0.100	−0.060	−0.005	+0.030	−0.120	−0.200
	3	0.410	−0.010	+0.050	0	0	+0.100	−0.060	−0.005	+0.030	+0.120	+0.100
	4	0.555	−0.010	+0.050	0	0	+0.100	−0.060	−0.005	+0.030	−0.120	−0.200
	5	0.727	−0.010	+0.050	0	0	+0.100	−0.060	−0.005	+0.030	+0.120	+0.100
	6	0.858	−0.010	+0.050	0	0	+0.100	−0.060	−0.005	+0.030	−0.120	−0.200
5 °C min^{-1}	1	0.397	0	0	−0.060	+0.010	+0.100	−0.060	+0.005	−0.030	+0.120	+0.100
	2	0.523	0	0	−0.060	+0.010	+0.100	−0.060	+0.005	−0.030	−0.120	−0.200
	3	0.673	0	0	−0.060	+0.010	+0.100	−0.060	+0.005	−0.030	+0.120	+0.100
	4	0.823	0	0	−0.060	+0.010	+0.100	−0.060	+0.005	−0.030	−0.120	−0.200
	5	0.932	0	0	−0.060	+0.010	+0.100	−0.060	+0.005	−0.030	+0.120	+0.100
	6	0.982	0	0	−0.060	+0.010	+0.100	−0.060	+0.005	−0.030	−0.120	−0.200
Best rate law		F1	R3	D4	D4	A3	F1	R2	R3	D4	F1	F1
SEE × 10^2		1.37	2.08	3.72	4.75	1.82	5.20	2.90	1.93	3.70	5.76	7.64
Second-best law		R3	F1	F1	D3	F1	R3	F1	F1	D3	R3	R3
SEE × 10^2		2.73	2.16	4.54	5.45	2.16	5.69	2.95	2.15	4.56	7.00	8.94

[a] Magnitude of the error required to cause a change in indicated rate law.

are to the 5 °C min^{-1} data set and the 10 °C min^{-1} set is unchanged, adding only 0.010 or subtracting 0.060 from each point results in rate laws other than F1 providing the best fit. Introducing error in α by addition results in the A3 rate law (with F1 being second best) and the introduction of error by subtraction results in a D4 best fit (D3 being second best). Second, when both data sets are altered by addition of error, no change in rate law is indicated when the error in α is 0.100. At a subtractive error of 0.060 to each data point, R2 is the indicated best-fitting rate law and F1 is the second best. When alternating errors of 0.100 are introduced into alternate data points in each set, the best-fitting rate law is still F1. This is also true when the errors of 0.100 and -0.200 are introduced into alternating data points.

Several conclusions can be drawn by considering the data shown in Tables 2 and 3. It is obvious that the Reich and Stivala procedure provides a powerful, versatile method for determining the mechanism of a solid state reaction from nonisothermal kinetic data. It is also evident that the method is highly resistant to certain types of errors, at least for the two reactions studied here. For example, adding as much as 0.100 to all the data points does not alter the indicated best-fitting rate law for either of the processes studied here. Subtracting as much as 0.060 (0.090 in one case) is required to change the rate law. If the errors are restricted to only one data set, adding at least 0.050 is required to change the indicated rate law. However, subtraction errors as small as 0.010 in one case (F1 case for the 10 °C min^{-1} run) cause a change in indicated rate law. Also, additive errors of 0.010 to the data for the 5 °C min^{-1} run in the F1 case result in a change in rate law best-fitting the data. Errors of this magnitude are entirely possible from sample-to-sample variations.

The first-order process studied seems to be somewhat more sensitive to errors in α than the A2 process. For example, in one case an error of 0.005 subtracted in one data set and the addition of that amount in the other results in a change in the best-fitting rate law to R3. These are extremely small errors and it is likely that any two consecutive runs could vary this much. With the errors introduced in other ways, alterations of 0.100 or greater are required to produce a change in the rate law. Errors of this magnitude are unlikely to occur with modern instrumentation.

It is possible that reactions having other mechanisms than those studied here might show different sensitivity to errors in α. Also, there are other permutations of ways to introduce the errors. Finally, other experimental data sets could have been selected to use as a basis for the calculations. As a result of these factors, this work is probably representative of the behavior of the Reich and Stivala method.

The rate law shown in eqn. (1) cannot represent the majority of the rate laws tested in the Reich and Stivala procedure. Consequently, this versatile method is the method of choice for analyzing TG data to determine mechanism. While the Reich and Stivala procedure can identify any rate law that a solid state reaction is likely to follow, it is, nonetheless, still subject to sample-to-sample variations. Therefore, it is still desirable to compare data for several runs to have confidence that the mechanism indicated is not an artifact of the data chosen. It is unlikely that sample-to-sample variation and equipment errors can be sufficiently controlled so that a single pair of runs at two heating rates will give a reliable determination of the mechanism. This situation also exists, of course, for other types of determinations, including isothermal methods [14–16]. When suitable data are available, the Reich and Stivala procedure reliably indicates the most likely mechanism.

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