# Kinetic Analysis of the Dehydration of Potassium bis(Oxalato)cuprate(II) Dihydrate

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The dehydration of potassium bis(oxalato)cuprate(II) dihydrate, $K_2([Cu(C_2O_4)_2] \cdot 2H_2O$, has been studied isothermally and nonisothermally using TG. To determine the rate law for this reaction, the data from isothermal studies were analyzed according to 17 different rate laws. The data from nonisothermal experiments were analyzed by the procedure of Reich and Stivala. It was found that while an Avrami (nucleation) rate law with $n = 2$ gives the best fit most frequently, considerable run to run variation exists for both types of experiments. There is general agreement on the most likely mechanism from isothermal and nonisothermal experiments, but the two methods were not consistent with respect to the next most likely mechanism. © 1990 Academic Press, Inc.

## Introduction

The difficulties associated with determining the mechanism of a reaction in the solid state are many and varied (*1*). Nonisothermal methods are typically applied to a rate law of the form

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

where the symbols have their usual meanings. However, $n$ is usually limited to values of 0, 1/3, 1/2, 2/3, . . . , 2 (*2*), although some iterative procedures allow any value of $n$ to be identified (*3*). Reich and Stivala have described a useful procedure for determining which of several rate laws is applicable by utilizing two different runs at heating rates differing by a factor of two (*4*). However, applying this method appears to give

inconsistent results in some cases when several runs are used because of sample to sample variations (*5, 6*).

As a part of a study on the effects of sample to sample variations in determining kinetic parameters using TG (*7, 8*), the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ was studied (*7*). It was found that for the reaction

$$K_2[Cu(C_2O_4)_2] \cdot 2H_2O(s) \rightarrow$$
$$K_2[Cu(C_2O_4)_2](s) + 2H_2O(g) \quad (2)$$
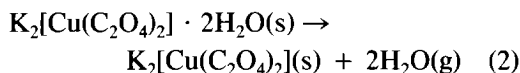
the best fit is obtained with $n = 2$ and the corresponding activation energy is $411.5 \pm 41.1 \text{ kJ mol}^{-1}$ (*7*). However, the decomposition of many hydrated compounds has been shown to follow a rate law of the type

$$[-\ln(1 - \alpha)]^{1/n} = kt, \qquad (3)$$

where $n = 1.5, 2,$ or $3$ (*9, 10*). To determine the rate law for this reaction, we have conducted an exhaustive study using both isothermal and nonisothermal kinetic methods. We have also carried out a comprehensive

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evaluation of the consistency of these kinetic methods with respect to the mechanism indicated.

## Experimental

The $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ used in this work was prepared by the method of Kirschner (11). The particles are of needle like or plate like structure. Kinetic studies on the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ were carried out both isothermally and nonisothermally using a Perkin–Elmer thermogravimetric system Model TGS-2. The isothermal experiments involved heating 3- to 7-mg samples in an atmosphere of dry nitrogen with a flow rate of 10 $cm^3$ $min^{-1}$. Mass loss was recorded as a function of time using scale expansion for more accurate reading and $\alpha$ was calculated by comparing the observed mass loss to that for the complete dehydration. The $(\alpha, t)$ data were fitted to 17 different rate laws using linear regression implemented on a microcomputer.

Nonisothermal kinetic studies were carried out employing previously reported procedures (12). Heating rates of 2.5, 5, and 10° $min^{-1}$ were used. Data from three runs at each heating rate were analyzed and calculations for mechanism were carried out using the Reich and Stivala procedure (4) implemented on a microcomputer.

The data from the nonisothermal experiments were also analyzed assuming that the rate law is given by Eq. (1) using the Coats and Redfern method (2) and the Reich and Stivala method (3). Calculations were carried out using a program written in BASIC implemented on a microcomputer.

## Results and Discussion

The dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ was found to take place in a single step when the reaction was studied both isothermally and nonisothermally using TG. Heating the compound in air on a hot stage microscope
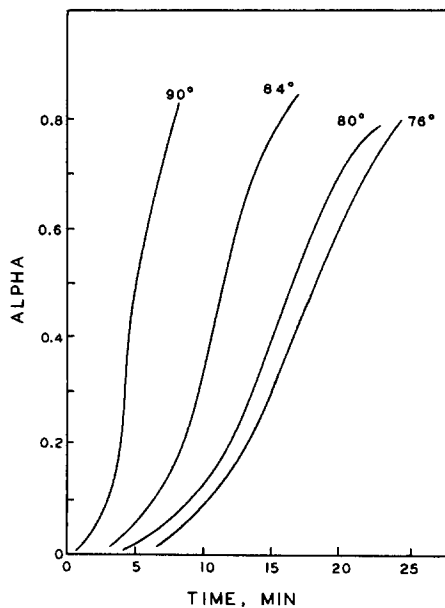


FIG. 1. Typical plots of $\alpha$ vs time for the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$.

shows that the individual particles retain their original structures throughout the dehydration. However, the material undergoes an obvious change in appearance from clear, blue, translucent crystals to a darker opaque appearance. Both types of crystals behaved similarly. When the dehydration was studied isothermally, it was found that the reaction could be followed conveniently at temperatures from 76 to 90°C. Figure 1 shows typical rate plots of $\alpha$ vs time for the reaction in this range of temperature. In order to determine the mechanism of this reaction, the $(\alpha, t)$ data were fitted to the 17 different rate laws shown in Table I. In analyzing the data, $\alpha$ values in the range 0.10 to 0.85 were used. Temperatures of 76, 80, 84, 86, and 90°C were used with four runs being made at each temperature.

The results shown in Table II indicate that for 13 out of 20 separate runs, either the best fit or the second best fit of the data was provided by the two-dimensional growth of

## TABLE I

RATE LAWS USED TO FIT THE ISOTHERMAL
KINETIC DATA

| $g(\alpha)$ | $g(\alpha)$ |
|---|---|
| $-\ln(1 - \alpha)$ | $1/(1 - \alpha)^*$ |
| $[-\ln(1 - \alpha)]^{2/3}$ | $[1/(1 - \alpha)]^{2*}$ |
| $[-\ln(1 - \alpha)]^{1/2}$ | $(1 - \alpha)\ln(1 - \alpha) + \alpha$ |
| $[-\ln(1 - \alpha)]^{1/3}$ | $[1 - (1 - \alpha)^{1/3}]^2$ |
| $1 - (1 - \alpha)^{2/3a}$ | $\alpha^2$ |
| $1 - (1 - \alpha)^{1/2}$ | $[\ln(1 - \alpha)]^{1/4}$ |
| $\ln[\alpha/(1 - \alpha)]^a$ | $\alpha^{1/2}$ |
| $\ln \alpha^a$ | $(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$ |
| $1 - (1 - \alpha)^{1/3}$ | |

[a] Not tested in the Reich and Stivala procedure (4).
See M. E. Brown and C. A. R. Phillpots, *J. Chem. Educ.* **55**, 556 (1978) for processes.

nuclei, $A2$: $[-\ln(1 - \alpha)]^{1/2}$, rate law. This is also known as the Avrami–Erofeev rate law with an index of 2. Twelve runs gave the best fit with that rate law and one run

indicated that rate law for the second best fit. Five runs gave the best fit with the three-dimensional growth of nuclei, $A3$: $[-\ln(1 - \alpha)]^{1/3}$, rate law (Avrami–Erofeev with index of 3), and another eight indicated that rate law as the second best fit including six of the runs which gave the best fit with the $A2$ rate law. The only other rate law that gave a best fit or second best fit rather frequently was the $A1.5$: $[-\ln(1 - \alpha)]^{2/3}$ case. For that rate law, two runs gave it as the best fit and six runs gave it as the second best fit. The second best fitting rate law is also considered because there was usually only a very slight difference in correlation coefficients between the two best fitting rate laws. In most cases, the third best fitting rate law gave a correlation coefficient that was significantly lower than the two better fitting ones. Considering all of these results, it appears that the reaction should be considered as following an Avrami–Erofeev mech-

## TABLE II

RESULTS OF FITTING THE ISOTHERMAL $\alpha$ $t$ DATA TO 17 RATE LAWS

| Temperature (°C) | Run | Best/fit Rate law | $r$ | Second best fit Rate law | $r$ |
|---|---|---|---|---|---|
| 76 | 1 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99962 | $[-\ln(1 - \alpha)]^{2/3}$ | 0.99837 |
| | 2 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99971 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99868 |
| | 3 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99839 | $[-\ln(1 - \alpha)]^{1/4}$ | 0.99794 |
| | 4 | $[-\ln(1 - \alpha)]^{1/4}$ | 0.99976 | $\alpha^{1/2}$ | 0.99931 |
| 80 | 1 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99961 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99901 |
| | 2 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99959 | $[-\ln(1 - \alpha)]^{1/4}$ | 0.99851 |
| | 3 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99990 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99838 |
| | 4 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99982 | $[-\ln(1 - \alpha)]^{1/4}$ | 0.99868 |
| 84 | 1 | $[-\ln(1 - \alpha)]^{2/3}$ | 0.99700 | $1 - (1 - \alpha)^{1/3}$ | 0.99683 |
| | 2 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99977 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99906 |
| | 3 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99901 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99900 |
| | 4 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99982 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99870 |
| 86 | 1 | $[-\ln(1 - \alpha)]^{2/3}$ | 0.99854 | $1 - (1 - \alpha)^{1/3}$ | 0.99840 |
| | 2 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99929 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99855 |
| | 3 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99868 | $[-\ln(1 - \alpha)]^{2/3}$ | 0.99802 |
| | 4 | $[-\ln(1 - \alpha)]^{1/3}$ | 0.99978 | $[-\ln(1 - \alpha)]^{1/4}$ | 0.99856 |
| 90 | 1 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99995 | $1 - (1 - \alpha)^{2/3}$ | 0.99878 |
| | 2 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99991 | $1 - (1 - \alpha)^{2/3}$ | 0.99871 |
| | 3 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99993 | $1 - (1 - \alpha)^{2/3}$ | 0.99876 |
| | 4 | $[-\ln(1 - \alpha)]^{1/2}$ | 0.99994 | $1 - (1 - \alpha)^{2/3}$ | 0.99844 |

TABLE III

RATE CONSTANTS FOR THE DEHYDRATION OF $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ (AVRAMI–EROFEEV) RATE LAW WITH $n = 2$

| Temperature (°C) | $k \ (min^{-1})^a$ |
|---|---|
| 76 | 0.0493 ± 0.0014 |
| 80 | 0.0768 ± 0.0057 |
| 84 | 0.1127 ± 0.0074 |
| 86 | 0.1420 ± 0.0219 |
| 90 | 0.2369 ± 0.0136 |

[a] Shown as mean values ± standard deviation.

anism with an index of 2, especially in view of the fact that 12 runs gave the best fit with that rate law and only five gave the best fit with the $A3$ rate law.

With the dehydration having been established as following an Avrami–Erofeev mechanism with an index of 2, the rate constants shown in Table III were calculated. Using linear regression, these rate constants were fitted to the Arrhenius equation yielding an activation energy of $116 \pm 4$ kJ mol$^{-1}$ and a frequency factor of $1.12 \times 10^{16}$ min$^{-1}$.

Reich and Stivala have described a useful method for determining which of several rate laws is applicable to a solid state process ($4$). Since that method requires $\alpha$ values obtained at the same temperatures when the heating rates differ by a factor of two, TG runs were made at 2.5, 5, and 10° min$^{-1}$. However, $\alpha$ values could not be determined at the same temperatures for all these runs. Consequently, $\alpha$ values were determined for one range of temperatures for heating rates of 5 and 10° min$^{-1}$ and a different range of temperatures for heating rates for 2.5 and 5° min$^{-1}$. These data are shown in Table IV.

Since three runs are included at both 5 and 10° min$^{-1}$, there are nine combinations of runs at these heating rates differing by a factor of two. Similarly, there are nine combinations of the runs at 2.5 and 5° min$^{-1}$. Analysis of the 18 combinations of runs gave the results shown in Table V. Both the best fitting and the second best fitting rate laws are shown in Table V. Most of the combinations gave a significant difference between these two best fitting rate laws, but a few did not. Therefore, it is of interest to list both the best fitting and second best fitting rate laws.

Seven of the combinations gave the best

TABLE IV

VALUES OF $\alpha$ FOR HEATING RATES OF 2.5, 5 AND 10° MIN$^{-1}$

| Heating rate (°min$^{-1}$) | Run | $\alpha$ | | | | | |
|---|---|---|---|---|---|---|---|
| | | 103°C | 104°C | 105°C | 106°C | 107°C | 108°C |
| 10 | 1 | 0.095 | 0.127 | 0.165 | 0.209 | 0.260 | 0.312 |
| | 2 | 0.178 | 0.230 | 0.277 | 0.334 | 0.389 | 0.456 |
| | 3 | 0.131 | 0.165 | 0.211 | 0.252 | 0.301 | 0.355 |
| | 1 | 0.651 | 0.735 | 0.799 | 0.865 | 0.908 | 0.943 |
| 5 | 2 | 0.686 | 0.763 | 0.827 | 0.882 | 0.920 | 0.951 |
| | 3 | 0.598 | 0.683 | 0.757 | 0.827 | 0.878 | 0.919 |
| | | 97°C | 98°C | 99°C | 100°C | 101°C | 102°C |
| | 1 | 0.212 | 0.275 | 0.340 | 0.421 | 0.513 | 0.579 |
| 5 | 2 | 0.226 | 0.303 | 0.358 | 0.450 | 0.520 | 0.610 |
| | 3 | 0.144 | 0.203 | 0.261 | 0.343 | 0.410 | 0.509 |
| | 1 | 0.497 | 0.591 | 0.688 | 0.773 | 0.853 | 0.912 |
| 2.5 | 2 | 0.490 | 0.591 | 0.691 | 0.781 | 0.857 | 0.918 |
| | 3 | 0.666 | 0.764 | 0.848 | 0.912 | 0.953 | 0.975 |

TABLE V

RESULTS OF THE REICH AND STIVALA METHOD TO DETERMINE MECHANISNM

| Run combination | | Best fit | | Second best fit | |
|---|---|---|---|---|---|
| $10° \ min^{-1}$ | $5° \ min^1$ | Rate law | SEE[a] | Rate law | SEE[a] |
| 1 | 1 | $[-\ln(1-\alpha)]^{1/4}$ | 0.1286 | $\alpha^{1/2}$ | 0.2504 |
| 1 | 2 | $[-\ln(1-\alpha)]^{1/4}$ | 0.1063 | $\alpha^{1/2}$ | 0.2733 |
| 1 | 3 | $[-\ln(1-\alpha)]^{1/4}$ | 0.1692 | $\alpha^{1/2}$ | 0.2092 |
| 2 | 1 | $[-\ln(1-\alpha)]^{1/2}$ | 0.0721 | $\alpha^{1/2}$ | 0.0736 |
| 2 | 2 | $\alpha^{1/2}$ | 0.0946 | $[-\ln(1-\alpha)]^{1/2}$ | 0.0954 |
| 2 | 3 | $[-\ln(1-\alpha)]^{1/2}$ | 0.0316 | $\alpha^{1/2}$ | 0.0389 |
| 3 | 1 | $\alpha^{1/2}$ | 0.1673 | $[-\ln(1-\alpha)]^{1/2}$ | 0.1827 |
| 3 | 2 | $\alpha^{1/2}$ | 0.1901 | $[-\ln(1-\alpha)]^{1/4}$ | 0.1906 |
| 3 | 3 | $\alpha^{1/2}$ | 0.1261 | $[-\ln(1-\alpha)]^{1/2}$ | 0.1415 |
| $5° \ min$ | $2.5° \ min^{-1}$ | | | | |
| 1 | 1 | $[-\ln(1-\alpha)]^{2/3}$ | 0.0094 | $1-(1-\alpha)^{1/2}$ | 0.0747 |
| 1 | 2 | $[-\ln(1-\alpha)]^{2/3}$ | 0.0062 | $1-(1-\alpha)^{1/2}$ | 0.0789 |
| 1 | 3 | $[-\ln(1-\alpha)]^{1/2}$ | 0.0325 | $[-\ln(1-\alpha)]^{2/3}$ | 0.1352 |
| 2 | 1 | $[-\ln(1-\alpha)]^{2/3}$ | 0.0316 | $1-(1-\alpha)^{1/2}$ | 0.0522 |
| 2 | 2 | $[-\ln(1-\alpha)]^{2/3}$ | 0.0295 | $1-(1-\alpha)^{1/2}$ | 0.0534 |
| 2 | 3 | $[-\ln(1-\alpha)]^{1/2}$ | 0.0127 | $[-\ln(1-\alpha)]^{2/3}$ | 0.1106 |
| 3 | 1 | $[-\ln(1-\alpha)]^{1/2}$ | 0.0282 | $\alpha^{1/2}$ | 0.0483 |
| 3 | 2 | $[-\ln(1-\alpha)]^{1/2}$ | 0.0229 | $\alpha^{1/2}$ | 0.0488 |
| 3 | 3 | $[-\ln(1-\alpha)]^{1/2}$ | 0.1337 | $\alpha^{1/2}$ | 0.1410 |

[a] Standard error of estimate.

fit with the $A2$ rate law, and three more indicated that rate law as the second best fit. However, four combinations indicated a best fit with the $P3$: $\alpha^{1/2}$ rate law, and eight others indicated that rate law as the second best fit. A few combinations also indicated the best fit with either the $A1.5$ or the $A4$ rate law. Since the largest number of combinations indicate the $A2$ rate law as the best fit, it is likely that this is the appropriate mechanism in agreement with the isothermal studies. Thus, both isothermal and nonisothermal methods indicate the same mechanism but not with equal frequency. There is, however, a significant difference between the two methods in the second best fitting rate law. Isothermal experiments indicate the second best fitting rate law to be $A3$ while nonisothermal studies indicate $P3$. The reasons for this difference are unclear.

It should be pointed out that the nonisothermal method requires the use of $\alpha$ values which are quite small in this case because of the difference in reaction rates when heating at 5 and $10° \ min^{-1}$. This may affect the results, but previous studies have shown that there may be no adverse effects (13, 14). Also it seems unlikely that the second best rate law would be altered but not the best fitting one. It appears that isothermal and nonisothermal methods are of about equal validity in determining the mechanism of this solid state reaction. We have studied other processes in which the nonisothermal method appears to indicate more consistently a single mechanism (15).

Because so many kinetic studies are carried out assuming a rate law of the form shown in Eq. (1), the data from the nonisothermal TG runs were analyzed by the Coats

TABLE VI
RESULTS OF ANALYSIS OF TG DATA USING RATE LAW SHOWN IN EQ. (1)

| Run | Heating rate (°C/min) | Coats and Redfern | | Reich and Stivala | |
|-----|-----|-----|-----|-----|-----|
| | | $n$ | $E$ (kJ/mol) | $n$ | $E$ (kJ/mol) |
| 1 | 10 | 2 | 329.3 | 2.07 | 334.9 |
| 2 | 10 | 2 | 327.8 | 2.36 | 356.0 |
| 3 | 10 | 2 | 304.7 | 2.07 | 309.4 |
| 4 | 5 | 5/3 | 361.9 | 1.84 | 388.8 |
| 5 | 5 | 2 | 389.3 | 2.15 | 394.1 |
| 6 | 5 | 2 | 420.6 | 1.88 | 410.6 |
| 7 | 2.5 | 5/3 | 402.5 | 1.73 | 419.1 |
| 8 | 2.5 | 5/3 | 412.8 | 1.53 | 398.3 |
| 9 | 2.5 | 5/3 | 444.0 | 1.72 | 462.2 |
| Ave. | | | $377 \pm 45.4$ | $1.93 \pm 0.24$ | $385.9 \pm 43.6$ |

and Redfern (2) and the Reich and Stivala (3) methods. While the isothermal kinetic studies and the nonisothermal procedure testing 12 rate laws indicate that the correct rate law is of the A2: $[-\ln (1 - \alpha)]^{1/2}$ form, it is interesting to apply rate law given in Eq. (1) to see how well it fits the data. This is especially true in view of the fact that such methods are regularly employed to determine kinetic parameters. The results of this analysis are shown in Table VI. The values for $n$ and $E$ agree well with those previously reported (8).

Several facts are immediately obvious from these results. The best fit occurs when an $n$ value of about 2 is used. This value is indicated by both methods. While the values are not shown, in every case a correlation coefficient of at least 0.998 or greater was found in the Coats and Redfern method. In some cases, the values were 1.000 to this number of decimal places. Obviously, an accurate mathematical representation of the data is afforded by Eq. (1) when $n = 2$ whether it provides any information about the mechanism or not. An equation of the form of Eq. (1) can represent only a few of the rate laws shown in Table I (e.g., first and second order, $1 - (1 - \alpha)^{1/3}$, etc.). Therefore, there is no way that analysis of

$(\alpha, T)$ data using methods based on Eq. (1) can identify a diffusion control or nucleation mechanism. Further, the true activation energy is about $116 \pm 4$ kJ mol$^{-1}$ while the values shown in Table VI are about four times this value. The value of $116 \pm 4$ kJ mol$^{-1}$ is typical of the values reported for the dehydration of CuSO$_4 \cdot$ 5H$_2$O ($104 \pm 10$ kJ mol$^{-1}$) (9) and other hydrated salts (10). Clearly, assuming that Eq. (1) gives the form of the rate law leads to an analysis of data that provides no useful kinetic information in this case.

Several conclusions, previously alluded to in various ways (5–8, 16, 17) are apparent from the results of this work. First, it is immediately obvious that neither an isothermal method nor the Reich and Stivala procedure can be counted on to indicate the mechanism unambiguously from limited data. It is not clear what the required number of experiments might be, but it seems certain that the more data available the greater the likelihood that a consistent mechanism can be established. Perhaps in some fortuitous cases procedural variables can be controlled to such an extent that such variations in mechanism indicated do not occur.

Second, when TG data are the basis for

analysis, isothermal and nonisothermal methods seem to be of about equal consistency in identifying a particular mechanism, at least for the reaction studied in this work. For example, in the 20 isothermal runs considered in this study, the $A2$ rate law was the best fitting or the second best fitting in 13 out of 20 cases. However, 10 out of 18 cases of the nonisothermal procedure indicated this rate law as the best fitting or second best fitting. These results might be different for some other reaction.

Third, in certain selected runs (both isothermal and nonisothermal), three or four rate laws fit the data almost equally well. In some cases, these rate laws represent drastically different physical processes. It is highly unlikely that the digit in the fourth or fifth decimal place in a correlation coefficient or SEE can really indicate whether a process is first order or a contracting volume.

Finally, the application of the rate law,

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

using the Coats and Redfern (2) and Reich and Stivala (3) procedures may provide an accurate mathematical fit to the data but no information about the actual mechanism of the reaction. There is a tendency to believe that nonisothermal methods are less reliable than isothermal ones (18). That certainly may be the case if the methods are based solely on a rate law like that shown in Eq. (1). However, the Reich and Stivala procedure testing 12 different rate laws appears to alleviate that condition. Perhaps these mechanisms, regardless of the computational procedure used to indicate them, should not be viewed as how the reactions actually occur in any concrete way. The indicated mechanism is undoubtedly an artifact of which data are included in the computation in many cases.

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