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AN ANALYSIS OF THE REICH AND STIVALA ALGORITHM FOR DETERMINING THE REACTION MECHANISM FROM TG DATA

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ABSTRACT

The mechanisms indicated by the Reich and Stivala algorithm were evaluated for the decomposition of $(NH_4)_2CO_3$, NH_4HCO_3, and *trans*-$[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O$. Different mechanisms are indicated when data from different TG runs are used. Also, the data points selected within the same two runs influence the type of mechanism that best represents the data. Apparently, sample-to-sample variations can preclude the unambiguous assignment of a mechanism.

INTRODUCTION

Solid state reactions may follow any of several possible mechanisms depending on what type of process (e.g., diffusion, nucleation etc). is rate controlling. It has recently been suggested that a computer-aided analysis of isothermal and non-isothermal TG data can distinguish one of 12 theoretically possible solid state mechanisms [1]. With two TG runs at different heating rates, the standard error of estimate (S.E.E.) was calculated for each theoretically possible rate law. The rate law giving the lowest S.E.E. was then presumed to represent the correct mechanism. It is required that the heating rates differ by a factor of two and that α values be determined at the same temperatures in each run. However, we have previously noted that rather wide variations occur from sample to sample TG runs making it difficult to determine reliable kinetic parameters when limited TG data are available [2]. Since the TG analysis to determine the mechanism only requires two TG curves for its application, it is of considerable interest to determine how sample-to-sample effects alter the mechanism indicated. Accordingly, we have studied the results of the mechanism determination using multiple TG runs for the decomposition of $(NH_4)_2CO_3$, NH_4HCO_3 and *trans*-$[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O$. The results of this work are presented in this report.

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EXPERIMENTAL

Compounds

Trans-$[Co(NH_3)_4Cl_2]HSO_4$ was prepared using the method of Schlessinger [3].

Trans-$[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O$ was prepared from the bisulfate using the method of Lobanov [4]. The bisulfate (2 g, 0.007 mol) was added to 80 ml of water at 0 °C and the solution was placed in an ice bath. Potassium bromate (10 g, 0.06 mol) was added to the cold solution and a precipitate of *trans*-$[Co(NH_3)_4Cl_2]BrO_4$ formed after cooling the solution. The green crystals were separated by filtration and washed with 50% ethanol, 95% ethanol, and ether, and allowed to dry in air.

The $(NH_4)_2Co_3$ and NH_4HCO_3 were reagent grade materials and were used without further treatment.

Thermal studies

TG studies were carried out with a Perkin–Elmer thermogravimetric system, model TGS-2. All the runs were made in a dry nitrogen atmosphere. Heating rates of 5, 10, and 20 °C min^{-1} were used. The procedures employed were similar to those previously described [5].

Calculations

The calculations to determine the indicated mechanism were carried out using the program of Reich and Stivala [1]. Calculations were carried out using a microcomputer.

RESULTS AND DISCUSSION

In order to determine the variation in indicated mechanism that might result using actual reaction data, three materials were chosen for study. The ammonium carbonate and ammonium bicarbonate decompose completely in one step and have previously been studied [6]. The reactions are

$$(NH_4)_2CO_3(s) \dashrightarrow 2NH_3(g) + H_2O(g) + CO_2(g) \qquad (1)$$

and

$$NH_4HCO_3(s) \dashrightarrow NH_3(g) + H_2O(g) + CO_2(g) \qquad (2)$$

These compounds were chosen because the decomposition results in complete mass loss and, therefore, α values can be determined accurately. Table 1 shows the α and T data for decomposition of the ammonium salts with the

TABLE 1

Degree of conversion values for the decomposition of $(NH_4)_2CO_3$ and NH_4HCO_3

T (K)	α			
	Run 1 [a]	Run 2 [b]	Run 3 [a]	Run 4 [b]
$(NH_4)_2CO_3$				
343	0.160	0.350	0.250	0.310
348	0.205	0.435	0.325	0.380
353	0.254	0.530	0.410	0.475
358	0.315	0.630	0.500	0.565
363	0.382	0.730	0.600	0.660
368	0.460	0.835	0.710	0.760
NH_4HCO_3				
363	0.193	0.310	0.255	0.305
368	0.275	0.415	0.350	0.410
373	0.363	0.530	0.449	0.520
378	0.465	0.650	0.570	0.645
383	0.585	0.780	0.680	0.770

[a] Heating rate is 10 °C min^{-1}.

[b] Heating rate is 5 °C min^{-1}.

middle range of the reaction being selected. The decomposition of *trans*-$[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O$ was also studied to contrast with that of the simple salts. Two steps of the decomposition were considered in this work. The first process is dehydration, and it takes place in the range 40–110 °C giving a 6.1% mass loss

$$trans\text{-}[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O(s) \longrightarrow trans\text{-}[Co(NH_3)_4Cl_2]BrO_3(s) + H_2O(g) \quad (3)$$

Decomposition occurs in the range 130–200 °C giving a mass loss of 43.4 ± 0.1% which corresponds to 142 mass units. The reaction thus appears to be

$$trans\text{-}[Co(NH_3)_4Cl_2]BrO_3(s) \longrightarrow CoCl_2Br(s) + 3NH_3(g) + 3H_2O(g) + \tfrac{3}{4}O_2(g) + \tfrac{1}{2}N_2(g) \quad (4)$$

Equation (4) corresponds to a loss of 143 mass units. Table 2 shows the α and T data for dehydration and decomposition of *trans*-$[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O$.

Analysis of the data shown in Table 1 to determine the mechanism gave the results shown in Table 3. From these results, several interesting observations can be made. Firstly, it can be seen that variations in the indicated probable mechanism are functions of two variables. These are the runs or data sets chosen and the acutal points chosen for inclusion. Additionally, it can be seen that vast differences in the indicated mechanism occur in the

TABLE 2

Degree of conversion for the decomposition of *trans*-$[Co(NH_3)_4Cl_2]BrO_3 \cdot H_2O$

T (K)	α		
	Run 1 [a]	Run 2 [b]	Run 3 [c]
Dehydration, eqn. (3)			
313	0.328	0.194	0.129
323	0.590	0.419	0.258
333	0.721	0.613	0.452
343	0.852	0.742	0.613
353	0.918	0.871	0.742
363	0.951	0.903	0.839
373	1.000	0.968	0.903
Decomposition, eqn. (4)			
423	0.055	0.027	0.018
428	0.073	0.041	0.027
433	0.101	0.050	0.031
438	0.138	0.068	0.040
443	0.188	0.104	0.049
448	0.252	0.140	0.066
453	0.317	0.194	0.093
458	0.408	0.158	0.124
463	0.532	0.311	0.164

[a] Heating rate is 5 ° C min^{-1}.
[b] Heating rate is 10 ° C min^{-1}.
[c] Heating rate is 20 ° C min^{-1}.

case of $(NH_4)_2CO_3$. However, the D3 mechanism, $\{1-(1-\alpha)^{1/3}\}^2$, was most often found for the decomposition of NH_4HCO_3.

The wide variety of theoretical kinetic models given as results in Table 3 shows that for experimentally obtained TG data, the Reich and Stivala method failed to determine consistently any one mechanism for either decomposition reaction. Unless one chooses the right data points for the

TABLE 3

Mechanisms indicated for the decomposition of $(NH_4)_2CO_3$ and NH_4HCO_3

Data used	Mechanism indicated	
	$(NH_4)_2CO_3$	NH_4HCO_3
Run 1 + Run 2	A1.5, $\{-\ln(1-\alpha)\}^{2/3}$	D1, α^2
Run 1 + Run 4	R3, $1-(1-\alpha)^{1/3}$	D3, $\{1-(1-\alpha)^{1/3}\}^2$
Run 3 + Run 2	D3, $\{1-(1-\alpha)^{1/3}\}^2$	D3, $\{1-(1-\alpha)^{1/3}\}^2$
Run 3 + Run 4	D3, $\{1-(1-\alpha)^{1/3}\}^2$	D3, $\{1-(1-\alpha)^{1/3}\}^2$
Run 3 + Run 2 [a]	D4, $1-(2\alpha/3)-(1-\alpha)^{2/3}$	D3, $\{1-(1-\alpha)^{1/3}\}^2$

[a] First and last data points were omitted for each run.

decomposition of $(NH_4)_2CO_3$ and NH_4HCO_3, the algorithm proved not to be useful as a tool to determine uniquely a mechanism. The cause of this failure lies in the sample-to-sample variation in the TG data.

While the data did not result in a single mechanism being indicated, the activation energies calculated using the expression [7]

$$E = RT_1T_2 \ln(\alpha_1/\alpha_2)/(T_1 - T_2) \qquad (5)$$

are in good agreement. For $(NH_4)_2CO_3$, the values for the four runs are 46.4, 52.3, 53.9, and 51.5 kJ mol^{-1} giving an average value of 51.0 ± 2.8 kJ mol^{-1}. In the case of NH_4HCO_3, the four runs yield values of 82.4, 79.1, 73.6, and 72.8 giving an average value of 77.0 ± 4.0 kJ mol^{-1}. These results are quite acceptable for several experiments on the same material. Thus, while there is failure to indicate a unique mechanism, satisfactory kinetic parameters can result.

Analysis of the data shown in Table 2 is much more satisfactory for the dehydration reaction. In this case, data from run 1 and run 2 or data from run 2 and run 3 resulted in an indicated D3 mechanism, $\{1-(1-\alpha)^{1/3}\}^2$. The same result was obtained using identical run combinations but with the last data point omitted from each set. Likewise, the same result was obtained when the first and last data points were omitted from each data set. No combination tested resulted in any other mechanism than D3 being indicated for the dehydration reaction.

For the decomposition of *trans*-$[Co(NH_3)_4Cl_2]BrO_3$ according to eqn. (4) the results were quite different. Using data from runs 1 and 2, the indicated mechanism was F1, $-\ln(1-\alpha)$, while data from runs 2 and 3 resulted in an indicated mechanism of D3, $\{1-(1-\alpha)^{1/3}\}^2$. Because of the nature of the reaction, the α values at some of the lower temperatures during the higher heating rates are very small. Accordingly, the effect of omitting the first four points from the data for runs 1 and 2 was evaluated. In this case, the analysis of the remaining data points resulted in an indicated mechanism which is R3, $1-(1-\alpha)^{1/3}$.

The results of this study show that the method of Reich and Stivala does not result in a unique indicated mechanism [1]. Certainly no claim was made by these workers that the method would perform in this way. Our continuing interest in the magnitude of sample-to-sample variation in TG work led us to examine real data to see how well the algorithm works. Clearly, the actual runs chosen for comparison and the actual data points selected can drastically influence the output. In the absence of other mechanistic information, these indicated mechanisms should not be taken literally. The mechanism is established only with respect to the data used.

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