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Note

ON THE EXPERIMENTAL EVALUATION OF A REICH AND STIVALA COMPUTER ALGORITHM BY HOUSE ET AL.

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INTRODUCTION

Recently, House et al. (HAL) [1] evaluated a computer algorithm proposed by the present authors [2] for the determination of reaction mechanism from TG data. This computer algorithm was devised to supplement a previously presented graphical method [3], in fact it afforded a more quantitative analysis of TG data for mechanism. Whereas the computer method allowed for the overall determination of mechanism based on the standard error of estimate values (S.E.E.), the graphical method can allow the estimation of mechanism at various individual temperatures (corresponding to values of α_1 and α_2). The aim of this study is to compare the experimental overall computer results obtained by HAL with results obtained by the present authors using the complementary graphical procedure, and to comment on the limitations of these graphical and computer procedures which HAL should have but did not observe.

RESULTS AND DISCUSSION

Some of the limitations of the computer (and graphical) procedure are mentioned in the following. Thus, it was clearly stated for the computer method [2], "It may be noted here that at the lower conversion values (less than 0.5) it becomes very difficult to differentiate the mechanisms denoted by D_2, D_3 and D_4. Thus, for the preceding mechanisms, conversion values above 0.5 become more meaningful in the determination of mechanism." (Remark 1). In the publication on graphical analysis [3], it was further stated, "From Fig. 1 it can be seen that the curves representing diffusion mechanism (Nos. 1–4) become readily distinguishable only at higher α_2 values." (Remark 2). It was also stated [3], "when accurate α_1, α_2, and temperature values are employed, the plot depicted in Fig. 1 ... can provide corroborative support for certain solid-state mechanisms determined from

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TABLE 1

Graphical estimation of mechanism from α values for the decomposition of $(NH_4)_2CO_3$ and NH_4HCO_3 [1]

T (K)	Runs used			
	(1+2) [a]	(1+4) [a]	(3+2)	(3+4)
$(NH_4)_2CO_3$				
343	–	–	– [a]	– [a]
348	–	–	– [a]	– [a]
353	–	–	D3	D3 [b]
358	–	–	D3	D3 [b]
363	–	–	D3	D3 [b]
368	–	–	D3	D3 [b]
NH_4HCO_3				
363	–	–	– [a]	– [a]
368	–	–	D3 [b]	D3 [b]
373	–	–	D3 [b]	D3 [b]
378	–	–	D3 [b]	D3 [b]
383	–	–	D3 [b]	D3 [b]

[a] See Remarks 1 and 2 in text; most α values in Run 1 were low (< 0.5).

[b] See Remark 4 in text.

non-isothermal TG data by other procedures previously described" (Remark 3).

In order to illustrate the difficulty in obtaining an unambiguous determination of a D mechanism when α values below 0.5 are employed (HAL determined that a D-type mechanism obtained using many α values below 0.5), the following low values of α_2 and α_1 are presented for the D mechanisms in the order, D_2, D_4 and D_3, respectively: 0.143, 0.200, 0.143, 0.200, 0.144, 0.200; 0.216, 0.300, 0.217, 0.300, 0.219, 0.300; 0.290, 0.400, 0.292, 0.400, 0.297, 0.400. From the preceding, it is readily apparent that at low values of α_2 (and/or α_1), for the same value of α_1, the values of α_2 are almost identical for the three D mechanisms mentioned (this indicates the importance of Remarks 1–3).

From temperature and conversion data obtained by HAL [1], Tables 1 and 2 were constructed using the graphical method of analysis previously noted [3]. Besides Remarks 1–3, we may also state that in the utilization of the graphical method (and of the computer method), even when points determined by the $\alpha_1 - \alpha_2$ values do not lie on the D_3 curve but lie directly below this curve (which is lower on the graph than curves representing other mechanisms considered) then the probable mechanism will still be D_3 (similar considerations apply to the S.E.E. values used in the computer procedure) (Remark 4).

Table 1 portrays mechanisms obtained graphically for the decomposition of $(NH_4)_2CO_3$ (AC) and NH_4HCO_3 (AB). In the case of AC for Runs

TABLE 2

Graphical estimation of mechanism from α values for the dehydration and decomposition of $[CO(NH_3)_4Cl_2]BrO_3 \cdot H_2O$ [1]

T (K)	Runs used	
	(1+2)	(2+3)
Dehydration		
313	– [a]	– [a]
323	– [a]	– [a]
333	D3 [b]	D2
343	D3 [b]	D3 [b]
353	D3	D3
363	D3 [b]	D3 [b]
373	– [c]	D3
Decomposition		
423	– [c,d]	– [c,d]
428	– [c,d]	– [c,d]
433	– [c,d]	– [c,d]
438	– [c,d]	– [c,d]
443	F1	– [c,d]
448	F1	– [c,d]
453	F1/D1	F1/R3
458	F1/D1	F1/R3
463	F1	F1

[a] See remarks 1 and 2 in text.

[b] See Remark 4 in text.

[c] Values beyond range of curves.

[d] Slopes of curves very steep at these very low α values.

(3 + 2) and (3 + 4), mechanistic designations were left blank at 343–348 K. In view of the indication of a D mechanism (D3) at 353–368 K, values of α at 343–348 K were considered to be too low to obtain an unambiguous D mechanism (cf. Remarks 1 and 2). Further for Run (3 + 4) at 353–368 K, Remark 4 was found to hold. Values of α for Run 1 were also considered to be too low for a D mechanism to be determined unequivocally. Thus, designations at 343–368 K for Runs (1 + 2) and (1 + 4) have not been included. Further a comparison of α-values between Runs 1 and 3 (10 °C min^{-1}) showed a wide discrepancy which was not explained by HAL (nevertheless, if values from Run 1 are used, then for Run (1 + 2), either an A1.5 or R2 mechanism is indicated while for Run (1 + 4) an R2 or R3 is indicated). In the case of AB, again most of the α values for Run 1 were considered too low (< 0.5) to yield an unambiguous D mechanism (which was indicated in Runs (3 + 2) and (3 + 4)). Further, as for AC, experimental α values for Runs 1 and 3 for AB were found to vary widely at 10 °C min^{-1}; again, there was no explanation of such a deviation by HAL (nevertheless, when these values were used for AB, Runs (1 + 2) and (1 + 4) afforded

either an α_2 or D2 designation at the various temperatures). Many of the graphical results obtained in the preceding are in agreement with those obtained by HAL using the computer method.

In Table 2, mechanistic designations are given for the dehydration and resulting decomposition of *trans*-$[CO(NH_3)_4Cl_2]BrO_3 \cdot H_2O$ [1]. As in the case of AB and AC in Table 1, the dehydration mechanism appears to be essentially D3 (except for D2 for Run (2 + 3) at 333 K). Thus, values of α at 313–323 K for Runs (1 + 2) and (2 + 3) were considered to be too low (< 0.5). HAL also found that a D3 mechanism was indicated using the complementary computer method. For the decomposition reaction, quite different results were obtained. At 423–438 K for Runs (1 + 2) and (2 + 3), α values were very low (< 0.15) to allow for an accurate determination of mechanism. From fig. 1 of ref. 3, it can be seen that at such low α values, the curves possess very steep slopes and their separation is relatively small. Although many of the α values given for Runs 2 and 3 were well below 0.2, the graphical method did indicate that most of the mechanisms could be F1 for Run (1 + 2) between 443 and 463 K. At 453–463 K for Run (2 + 3), either an F1 or R3 mechanism was possible. HAL also indicated that an F1 mechanism was obtained for Run (1 + 2), while data from Run (2 + 3) resulted in a D3 mechanism. It should also be noted here that for such low α values, the utilization of the computer method would be invalid (beyond the range of values used to correlate data via computer).

CONCLUSIONS

The results of our examination of the HAL work by means of graphical analysis indicate the following. Since a D3 mechanism was apparent for the decomposition of AB or AC, precautions should have been taken by HAL to employ α values > 0.5 as much as possible (see Remarks 1 and 2 in text). If necessary, additional runs should have been made with this limitation in mind. Further, values of α obtained by HAL for the decomposition of AB or AC in Run 1 were in poor agreement with those values obtained in Run 3 even though both runs were carried out under identical temperatures and heating rates. Obviously, such a wide discrepancy in α values can lead to results wherefrom more than one mechanism can be obtained. In the case of the inorganic cobalt derivative used by HAL, very low values of α were used (most were below 0.2). HAL admitted that due to the nature of the reaction, the α values at some of the lower temperatures during the higher heating rates are very small. At these low values, the slopes of various pertinent curves are very steep and the curves are less separated, making an accurate determination of mechanism more difficult. Also, such low α values can be outside of the range of the curves. Finally, as indicated in Remark 3, the procedure and data used by HAL would be more appropriate for corroborative purposes, especially when α values are not of a high degree of accuracy.

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