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Note

A REPLY CONCERNING THE REICH AND STIVALA COMPUTER ALGORITHM TO DETERMINE MECHANISM

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We were not unaware of the limitations and suggestions made by Reich and Stivala regarding the application of their algorithm to determine mechanism [1] In this connection, " 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 Since the TG analysis to determine mechanism requires only two TG curves for its application, it is of considerable interest to determine how sample-to-sample effects alter the mechanism indicated" [2] Our primary interest was, therefore, to determine the extent to which different samples influence the output, not to show that the Reich and Stivala method does not work

While Reich and Stivala point out that " conversion values above 0.5 become more meaningful ," two of our runs with $(NH_4)_2CO_3$ and two with NH_4HCO_3 start with $\alpha > 0\,3$ The intent of "more meaningful" is not definitive Examination of the data in table 1 of ref 2 shows that this was necessary in order to get significant overlap of the α ranges due to sample-to-sample variation In that study we made no attempt to run a large number of samples in order to find runs that agree Our aim was to use the results as they are normally encountered In the case of dehydration of *trans*-$[Co(NH_3)_4Cl_2]BrO_3\ H_2O$, the data in table 2 of ref 2 show that in the first run only one point had $\alpha < 0\,5$, the second run had only two points with $\alpha < 0\,5$, and the third run had only three points with $\alpha < 0.5$. The decomposition reaction was quite different owing to the greatly different behavior of the reaction at different heating rates Again, our study was undertaken to show sample-to-sample variations, not the loss of meaning when α is less than 0 5

After much discussion of various "remarks," it is interesting that for the decomposition of $(NH_4)_2CO_3$ and NH_4HCO_3 Reich and Stivala [1] conclude with, "Many of the graphical results obtained in the preceding are in agreement with those obtained by HAL using the computer method " It seems that the limitations imposed do not invalidate the method and that was not our objective Rather, it was to study sample-to-sample variations

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Analysis of our data for the dehydration of *trans*-$[Co(NH_3)_4Cl_2]BrO_3$ H_2O by Reich and Stivala [1] yields the conclusion, " the dehydration mechanism appears to be essentially D3 " "HAL also found a D3 mechanism was indicated using the complementary computer method " Also for the decomposition reaction our work indicated that F1 and R3 possibilities could result, which the Reich and Stivala graphical procedure [1] also indicated Thus, while there was no attempt to apply the method of Reich and Stivala in its most advantageous range in our investigation of sample-to-sample variations, most of our results agree with those so obtained

REFERENCES

1 L Reich and S S Stivala, Thermochim Acta, 130 (1988) 381
2 J E House, Jr , R J Webb, K A Kemper and H M Fogel, Thermochim Acta, 118 (1987) 261