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Note

COMPUTER ANALYSIS OF NON-ISOTHERMAL TG DATA FOR MECHANISM AND ACTIVATION ENERGY. PART III

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In Part I of this series [1], a so-called $p(x)$ function was employed as part of a computer program (CP) to distinguish one of ten theoretically possible solid-state decomposition mechanisms and to determine the corresponding activation energy (E), using non-isothermal (NI) TG data. Further, a truncated Schlömilch expansion [2] was used to estimate values of $p(x)$. Excellent agreement was obtained between calculated and reported results. In this paper, the previously reported CP [1] will be modified and generalized so that various expressions previously reported [3,4] can also be utilized to afford satisfactory results for E and mechanism.

THEORY

In general, for NI TG data

$$d\alpha/dT = [A/(RH)] \exp(-X) f(\alpha) \tag{1}$$

where $X = E/RT$; α = fractional conversion; A = pre-exponential factor; RH = constant heating rate; T = temperature (K); R = gas constant; and $f(\alpha)$ = some function of α which is dependent on mechanism. By using eqn. (1) in conjunction with various expressions previously reported, i.e., eqns. (2) and (6) of ref. 3 (E3) and eqns. (1), (2), (5)–(7) of ref. 4 (E4), it can be readily shown that, in general,

$$\log[g(\alpha)j(X)/f(X)] + X = \log[AE/(RH)R] = \text{constant} \tag{2}$$

where, $g(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$; $j(X) = aX^2 + bX$; and $f(X)$ = last terms in parentheses in E3 and E4 which involve functions of X, e.g., for eqn. (5), $f(X) = 1 - 2/X + 6/X^2$ (a truncated integration by parts expansion). For E3 and eqns. (1), (2) and (6) of Ref. 4, $a = 0$, $b = 1$ in $j(X)$; for eqn. (5), $a = 1$, $b = 0$; for eqn. (7), $a = 1$, $b = 1$.

In order to apply eqn. (2) to the CP previously described and listed [1], the following modifications in the CP should be made. In line 30, change the

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F-value to 1.000; in line 35, use DEF FN P(X) to define the function f(X); and, in line 80, use B(K) = FN W[W(K)] + X + log[j(X)] − log[FN P(X)].

RESULTS AND DISCUSSION

Equation (2) was tested using NI TG data previously reported [1]. Thus, by using $f(X) = 1 - 2/X + 6/X^2$, $j(X) = X^2$ (cf. eqn. 5 of ref. 4), and the modified CP, results obtained for E (kcal mol^{-1}), and mechanism, and whether the computer analysis was complete (Y or N) are listed in order followed by the data line number [1] and the type of data used, respectively: 29, F1, Y, 185, Zsako complex I; 26, R3, Y, 195, Zsako complex II; 22, R3, Y, 205, sodium bicarbonate; 30, D2, Y, 215, Heide's theoretical data; 28, R2, N, 230, Reich's theoretical data; 30, D3, Y, 240, Reich's theoretical data. The preceding results agree exactly with those previously reported [1].

A typical printout (for the sake of brevity, the initial E-value used was 28 kcal mol^{-1}) of results obtained using NI TG data from line 240 and eqn. (5) of ref. 4 is given in the Appendix. Equation (2) of ref. 4 was also tested using NI TG data from line 240. Results obtained for E and mechanism were in excellent agreement with anticipated results. From the preceding, it may be safely assumed that the similar application of various other expressions in refs. 3 and 4 will also afford excellent results. Further, whereas the E-range used in Part I of this series [1] was limited to 20–30 kcal mol^{-1}, this range can now be extended (cf. ref. 4).

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APPENDIX

Results obtained for E and mechanism using reported TG data [1] and a computer program which uses the generalized eqn. (2).

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FOR A4: (-LN(1-A))^(1/4), DELTA= 1.6356
FOR A3: (-LN(1-A))^(1/3), DELTA= 1.5415
FOR A2: (-LN(1-A))^(1/2), DELTA= 1.3532
FOR R2: 1-(1-A)^(1/2), DELTA= .9551
FOR R3: 1-(1-A)^(1/3), DELTA= .9029
FOR F1: -LN(1-A), DELTA= .7899
FOR D1: A^2, DELTA= .308
FOR D2: A+(1-A)LN(1-A), DELTA= .143
FOR D4: 1-(2A/3)-(1-A)^(2/3), DELTA= .0767
FOR D3: (1-(1-A)^(1/3))^2, DELTA= .1124

PROB.MECHNSM.= D4: 1-(2A/3)-(1-A)^(2/3) FOR EA= 28 K/M

FOR A4: (-LN(1-A))^(1/4), DELTA= 1.6982
FOR A3: (-LN(1-A))^(1/3), DELTA= 1.6041
FOR A2: (-LN(1-A))^(1/2), DELTA= 1.4158
FOR R2: 1-(1-A)^(1/2), DELTA= 1.0177
FOR R3: 1-(1-A)^(1/3), DELTA= .9655
FOR F1: -LN(1-A), DELTA= .8523
FOR D1: A^2, DELTA= .3623,
FOR D2: A+(1-A)LN(1-A), DELTA= .1914
FOR D4: 1-(2A/3)-(1-A)^(2/3), DELTA= .116
FOR D3: (1-(1-A)^(1/3))^2, DELTA= .0498

PROB.MECHNSM.= D3: (1-(1-A)^(1/3))^2 FOR EA= 29 K/M

FOR A4: (-LN(1-A))^(1/4), DELTA= 1.7608
FOR A3: (-LN(1-A))^(1/3), DELTA= 1.6666
FOR A2: (-LN(1-A))^(1/2), DELTA= 1.4784
FOR R2: 1-(1-A)^(1/2), DELTA= 1.0803
FOR R3: 1-(1-A)^(1/3), DELTA= 1.0281
FOR F1: -LN(1-A), DELTA= .9148
FOR D1: A^2, DELTA= .4188
FOR D2: A+(1-A)LN(1-A), DELTA= .2463
FOR D4: 1-(2A/3)-(1-A)^(2/3), DELTA= .1698
FOR D3: (1-(1-A)^(1/3))^2, DELTA= .0128

PROB.MECHNSM.= D3: (1-(1-A)^(1/3))^2 FOR EA= 30 K/M

FOR A4: (-LN(1-A))^(1/4), DELTA= 1.8234
FOR A3: (-LN(1-A))^(1/3), DELTA= 1.7292
FOR A2: (-LN(1-A))^(1/2), DELTA= 1.541
FOR R2: 1-(1-A)^(1/2), DELTA= 1.1428
FOR R3: 1-(1-A)^(1/3), DELTA= 1.0907
FOR F1: -LN(1-A), DELTA= .9772
FOR D1: A^2, DELTA= .4769
FOR D2: A+(1-A)LN(1-A), DELTA= .3041
FOR D4: 1-(2A/3)-(1-A)^(2/3), DELTA= .2292
FOR D3: (1-(1-A)^(1/3))^2, DELTA= .0754

PROB.MECHNSM.= D3: (1-(1-A)^(1/3))^2 FOR EA= 31 K/M


EA= 30 KCAL/MOL FOR MECHNSM. D3: (1-(1-A)^(1/3))^2, DELTA= .0127929869

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