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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM DTA TRACES

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Recently, the authors presented [1] a procedure whereby kinetic parameters, activation energy (E) and reaction order (n), could be determined concurrently by the utilization of a single DTA trace. In this procedure, the lowest standard deviation obtained was used as the criterion in estimating final values of E and n. In the present paper, an iteration method is presented whereby values of E and n are obtained concurrently, by means of a computer, employing a previously reported criterion and a single DTA trace [2]. This procedure is then applied to the decomposition of benzenediazonium chloride (BDC), polyethylene (PE), and sodium bicarbonate (SB).

THEORY

Assuming an 'n-type' reaction and utilizing the corresponding well-known TG expression

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{RH}\exp\left(\frac{-E}{RT}\right)(1-\alpha)^n \qquad (1)$$

along with previously described approximate expressions [1], eqn. (1) can be converted to an expression applicable to a DTA trace

$$\ln\left[\left(\frac{\Delta T_1}{\Delta T_2}\right)\left(\frac{\tilde{a}_2}{\tilde{a}_1}\right)^n\right]=\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \qquad (2)$$

where $\tilde{a}=\int_T^{T_\infty}\Delta T\mathrm{d}T$. Equation (2) resembles eqn. (2) of ref. 2 so that a similar criterion for the estimation of E and n can be employed. Thus, briefly, values of n are incremented until the value of the intercept (theoretically zero) changes sign. At this point, the value of n (and its corresponding E/R value) is noted at the lower absolute value of the intercept, and considered to be the final value [2].

TESTING THE METHOD

The preceding method is initially applied to DTA data provided by Borchardt for the decomposition of BDC in aqueous solution at a heating rate of ca. 1°C min^{-1} [3]. Table 1 shows a computer printout wherein the data (line ♯370) is given in the order: ΔT (in), $\tilde{a}$(°C min) and T(°C). Following the data, values of the intercept, E/R and reaction order are given. Final values obtained for E (kcal mole^{-1}) and n are, respectively: 29.2 and 1.02. Assuming a first-order reaction, Borchardt obtained a value of $E = 28.3$ kcal mole^{-1} by graphical means. The agreement is considered to be satisfactory. (It may be noted here that two duplicate runs by Borchardt afforded values of E of 28.5 and 29.1 kcal mole^{-1}).

Polyethylene was subjected to thermal decomposition in the presence of

TABLE 1

Values of intercept, E/R and n from benzenediazonium chloride data [3]

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370 DATA 1.08,12.65,35,2.11,11.81,40,3.77,10.21,45,5.80,7.508,50,6.5,5.078,54,5.95,3.102,57,
3.03,.912,61.2: REM BORCHARDT THESIS, ØN2CL, 1-DEG/MIN, TABLE VII, P.90
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Intercept	E/R	Order, n
1.33654	36637.37	0.100001
1.19123	34242.32	0.200001
1.04592	31847.27	0.300001
0.90062	29452.22	0.400001
0.75531	27057.18	0.500001
0.61001	24662.13	0.600001
0.4647	22267.08	0.700001
0.31939	19872.03	0.800001
0.17409	17476.99	0.900001
0.02878	15081.94	1.000001
−0.11652	12686.89	1.100001

Initial values of intercept, E/R and n are, resp.: 0.02878, 15081.94 and 1.000001

0.17409	17476.99	0.900001
0.15956	17237.48	0.910001
0.14503	16997.98	0.920001
0.1305	16758.47	0.930001
0.11597	16518.97	0.940001
0.10143	16279.46	0.950001
0.0869	16039.96	0.960001
0.07237	15800.45	0.970001
0.05784	15560.95	0.980001
0.04331	15321.44	0.990001
0.02878	15081.94	1.000001
0.01425	14842.44	1.010001
−2.8E−04	14602.93	1.020001

Final values of intercept, E/R and n are, resp.: −2.8E−04, 14602.93 and 1.020001 nitrogen, by means of DTA, at a heating rate of ca. 8.7°C min^{-1} [4]. By using the preceding computer method, the values of E and n obtained were, respectively: 69 kcal mole^{-1} and 0.88. (Similar values could also be obtained for PE when a heating rate of ca. 16.1 min^{-1} was utilized). By using two DTA traces and graphical procedures for the same PE data, the values of E and n obtained were, respectively: 68 and 0.94 [4]. It should be noted here that all the preceding results obtained for PE are applicable only over an initial range of ca. 25–30% and above [4]. At much lower conversions, values of n of about zero have been reported [4,5]. Finally, when SB was thermally decomposed using DTA at a heating rate of ca. 3.5°C min^{-1} in the presence of still air, the values of E and n which resulted were, respectively: 24 kcal mole^{-1} and 0.60. By employing two DTA traces and graphical means, the values of E and n obtained were, respectively: 19 kcal mole^{-1} and 0.68 [6].

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