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Note

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

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Recently, the authors presented computer programs (CP) for the determination of mechanism and corresponding activation energy (E) utilizing non-isothermal TG data and ten theoretically possible solid-state decomposition mechanisms [1,2]. These CPs were successfully applied to experimental as well as theoretical TG data, and were intended primarily to supplant other procedures for the determination of mechanism and E, e.g., those which use linear correlation coefficients (r) and so-called "sensible" judgments or "reasonable values". Thus, for example, Dollimore and co-workers [3] recently investigated the decomposition kinetics of impure commercial magnesium hydroxide in still air using DTA (from which values of conversion and corresponding temperature were obtained). They determined that a Zhuralev rate expression was applicable based, among other things, on "sensible results". (Further, Dollimore et al. incorrectly stated that Mackenzie and Melling [4] had criticized the methods of Piloyan et al. [5] and Reich [6]. No such criticism occurred!)

Bagchi and Sen (B–S) [7] recently analyzed the TG data of Fong and Chen (F–C) [8] for magnesium hydroxide. They utilized differential and integral forms of rate equations which differed from the standard forms commonly employed. B–S determined that results for E and A (pre-exponential factor) obtained from the modified differential and the modified integral equations agreed best when diffusion-controlled mechanisms were employed. This agreement led B–S to conclude that the thermal dehydroxylation of magnesium hydroxide involved processes such as, D1–D4 (plus some other diffusion mechanisms). They decided that the best agreement for E and A occurred with the D4 mechanism (Ginstling–Brounshtein equation). When this mechanism was employed, "reasonable values" of E were obtained. However, Koch, Stilkerieg and Carlsen (K–S–C) [9] presented strong experimental evidence against the expressions used by B–S. Thus, K–S–C obtained non-isothermal results originating from more than 600 individual DTA experiments, involving 90 reactions of different orders and types in a variety of solvents. They found that the standard rate equations commonly used for non-isothermal TG afforded results for E (and A) in excellent agreement with results obtained from isothermal data whereas, one of the modified expressions, which was employed by B–S, afforded poor agreement. Thus, although the expressions used by B–S may possess a rational theoretical basis, these equations did not yield acceptable experimental values, according to K–S–C (this may be due to the necessity for a more accurate estimation of the so-called "reaction onset temperature" than realized).

Further, values of r have been employed, to a large extent, by various authors in conjunction with the Coats and Redfern (C–R) method [10] to ascertain mechanism (and corresponding E value). The utilization of r to determine mechanism from TG data was indicated by various workers to be unsatisfactory [11–14]. In this connection, F–C attempted to determine which of 17 possible decomposition rate expressions best fit their TG data for the thermal dehydroxylation of magnesium hydroxide by means of r values. They found that it was very difficult to ascertain a probable mechanism based on r values since at least half of the expressions tested afforded values of r above 0.995! They have listed extensive experimental values of conversion and corresponding temperature.

The aim of the present paper is to analyze the TG data of F–C by computer procedures [1,2] in order to discover whether a unique probable mechanism (and its corresponding E value) can be ascertained. These previously reported computer methods [1,2] were modified so that the E-range was extended to 6–95 kcal mol^{-1}, and the number of mechanisms tested was increased to include the "n-types", i.e., $n = 1.25$, 1.35, 1.50, 1.60, 1.75 and 2.00.

RESULTS AND DISCUSSION

In Table 1 results obtained from the computer analysis (CA) of TG data from F–C for magnesium hydroxide are presented (18 of the 21 data sets for trace 1 were used). From this table, it can be seen that the most probable mechanisms (based on low delta values) are: A4, A3 and $n = 1.50$ (Nos. 1, 2 and 9). However, the lower acceptable limit for E/RT, in order for the CA to be valid, is 10 so that the apparent predominance of the A4 mechanism becomes questionable. Also, although mechanisms D1, D2, D3 and D4 (Nos. 13–16) are associated with high E/RT values, i.e., above the upper valid limit of 60, the order of magnitude of delta is so much larger than for A3 or $n = 1.50$ that it is very unlikely that such mechanisms are relevant to the magnesium hydroxide TG data utilized. Thus, of the 16 possible mechanisms tested, the probable one is: A3 or $n = 1.50$ (based on delta and E/RT values). However, since the delta values of A3 and $n = 1.50$ are very close, it becomes very difficult to decide, on the basis of the CA alone, which mechanism is the most probable. Similar results were obtained when 13 data sets were employed. Thus, for these data sets, delta values of A4, A3 and $n = 1.60$ (the latter now possessed a lower delta value than $n = 1.50$) were, respectively: 0.0065, 0.0075 and 0.0082. Corresponding values of E and the E/RT range were similar as for the preceding CA which employed 18 data sets.

F–C utilized the method of C–R along with r values and found that the values of r, using trace 1, were 0.997 for A4, A3, A2 and F1, and 0.999 for $n = 1.50$ and 2.00. Thus, from r values alone, F–C indicated that it was very difficult to decide which was the most probable among the preceding six mechanisms due to the very close values of r. When F–C used Satava's method [15] for trace 1 TG data, the following r values were obtained: 0.998 for A4, A3, A2 and F1, and 0.999 for $n = 1.50$ and 2.00. Nevertheless, despite the closeness of the r values, F–C decided that the likely mechanism was $n = 1.50$ because the parameters obtained for other types of mechanisms were "unreasonable". From the preceding, it can be seen that the utilization of the CA was advantageous in that it allowed the large number of possible mechanisms to be reduced in a fairly objective manner to only two, based on the delta values obtained and on the E/RT range. From the preceding CA, however, it is apparent that further work will be necessary (e.g., isothermal experiments) before a final unique mechanism can be decided upon (the A4-mechanism should also be tested).

Finally, it may be mentioned that values of E obtained by the CA and by F–C using the C–R method for trace 1 were in excellent agreement. Thus,

TABLE 1

Results from a computer analysis [1] of magnesium hydroxide TG data [8] for mechanism and activation energy (E)

No.	Mechanism	Delta	E (kcal mol^{-1})	(E/RT) range
1	A4	0.0059	11	8–9
2	A3	0.0069	15	11–12
3	A2	0.0109	24	18–19
4	R2	0.0342	45	33–36
5	R3	0.0299	46	34–37
6	F1	0.0207	50	37–40
7	$n = 1.25$	0.0131	52	38–42
8	$n = 1.35$	0.0105	53	39–42
9	$n = 1.50$	0.0086	55	40–44
10	$n = 1.60$	0.0087	56	41–45
11	$n = 1.75$	0.0125	57	42–46
12	$n = 2.00$	0.0210	60	44–48
13	D1	0.0911	84	62–67
14	D2	0.0773	89	65–71
15	D4	0.0713	91	67–73
16	D3	0.0593	95	70–76

for example, for A3, corresponding E values were 15 and 15.2; for A2, 24 and 23.9; for $n = 1.50$, 55 and 55.3. Similar E values were obtained for trace 1 TG data when the CA results were compared with those obtained using the Satava method. It may be noted here that E values were also determined, using only 13 data sets of TG data from F–C for trace 1, by means of two other CA procedures [16,17]. These methods were limited to "n-type" decompositions. Values of n and E (kcal mol^{-1}) obtained, respectively, were: 1.35 and 1.48; 53 and 54.6.

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