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Note

A COMPARISON OF SAMPLE-TO-SAMPLE VARIATION IN KINETIC PARAMETERS OBTAINED BY DIFFERENT METHODS

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Analysis of data is becoming increasingly sophisticated in this day of microcomputers and programmable calculators. Creative science is sometimes equated with creative data analysis [1]. The analysis of TG curves to yield kinetic parameters is no exception and new methods appear frequently. Some of these methods involve the use of computers [2—8] and it is tempting to assume that the use of one of these methods yields more reliable kinetic parameters than some of the older methods [9—11]. One of the newest methods provides an iterative technique for determining n and E by using the equation

$$\ln\left[\frac{1-(1-\alpha_i)^{1-n}}{1-(1-\alpha_{i+1})^{1-n}}\left(\frac{T_{i+1}}{T_i}\right)^2\right] = -\frac{E}{R}\left(\frac{1}{T_i}-\frac{1}{T_{i+1}}\right) \quad (1)$$

and varying n until the intercept is closest to zero [2]. Correlation coefficients are ignored. Certainly this is one of the simplest and most compact of the computer methods. However, we have previously shown that the sample-to-sample variations may completely obscure the slight differences produced by different data analysis techniques [12]. The purpose of this work was to compare the sample-to-sample variations that result from the application of the Reich and Stivala method with those from the Coats and Redfern method.

EXPERIMENTAL

The results of decomposition studies on $(NH_4)_2CO_3$, NH_4HCO_3, and NH_4HF_2 have previously been reported where the data were analyzed by the Coats and Redfern method [12,13]. Also, a previous study reported the kinetic parameters for the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2\ H_2O$ [14]. The necessary α and T data for using eqn. (1) in the Reich and Stivala method were obtained from the same curves as were the previously published data. The program used in the Coats and Redfern method tested values of 0, 1/3, 2/3, 1, and 2 for n.

A program was written for the Reich and Stivala method for use on the Texas Instruments TI-59 programmable calculator. Up to 10 (α, T) data pairs can be used and, when using a printer, the analysis is self-running after data entry. Details of the program and its use will be available elsewhere [15].

RESULTS AND DISCUSSION

The computer method of Reich and Stivala has been shown to yield kinetic parameters that are in good agreement with those obtained by other methods [2]. This fact does not establish whether or not such methods are superior to conventional methods for a particular sample or in reducing the sample-to-sample variations in kinetic parameters. Certainly no claim was made that the computer method provided greater uniformity in derived values for *n* and *E* [2]. It is, however, of considerable interest to determine this since there is little question that the use of these computer methods will increase.

In order to compare adequately the magnitudes of sample-to-sample variations resulting when different methods of analysis are used, two completely different types of process were studied. Since a great many processes fall into the categories of decomposition and hydration, these types were selected. The decomposition of ammonium salts provides a useful comparison for decomposition and the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2\ H_2O$ is a convenient dehydration process [14]. Table 1 shows the results of carrying

TABLE 1

A comparison of results of the Coats and Redfern and the Reich and Stivala methods for analyzing TG data for the decomposition of ammonium salts

	Sample	Reich and Stivala		Coats and Redfern	
		Best *n*	*E* (kJ mole^{-1})	*n*	*E* (kJ mole^{-1})
$(NH_4)_2CO_3$	1	0.88	76.99	1	77.94
	2	1.79	89.95	2	89.80
	3	1.31	96.86	1	89.42
	4	2.38	111.79	2	100.68
	5	1.09	96.29	1	91.50
	Ave.	1.49	94.38		89.87
	σ	0.60	12.60		8.09
NH_4HCO_3	1	1.20	99.97	1	95.78
	2	1.32	90.68	3/4	77.81
	3	1.33	99.11	1	92.65
	4	1.06	80.62	1	76.70
	5	1.66	94.57	1	81.33
	Ave.	1.31	92.99	1	84.85
	σ	0.22	7.86		8.78
NH_4HF_2	1	0.38	73.77	2/3	70.61
	2	0.37	59.21	1/3	57.73
	3	0.47	64.81	2/3	61.69
	4	0.96	75.54	1	75.96
	5	0.46	65.06	2/3	68.65
	6	0.32	61.62	2/3	66.25
	Ave.	0.49	66.67	2/3	66.25
	σ	0.24	6.58		6.69

TABLE 2

A comparison of results of the Coats and Redfern and Reich and Stivala methods of analyzing TG data for the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2\ H_2O$

Sample	Reich and Stivala		Coats and Redfern	
	Best n	E (kJ mole^{-1})	n	E_n (kJ mole^{-1})
1	1.52	391.6	2	435.1
2	1.34	317.4	1	271.6
3	1.99	496.9	2	469.5
4	2.07	412.8	2	402.9
5	1.98	387.9	2	382.3
6	2.04	368.8	2	378.3
7	1.80	344.1	2	363.7
8	1.96	430.2	2	436.5
9	1.56	404.9	2	464.1
10	2.18	489.8	2	469.4
11	2.10	390.9	2	366.9
12	2.19	392.1	2	375.9
Ave.	1.89	402.3	2	401.3
σ	0.28	52.0		57.7

out the Reich and Stivala analysis on ammonium salts. The corresponding data for dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2\ H_2O$ are shown in Table 2. In these tables, the n of the Coats and Redfern method is not necessarily the "best" n. It is simply the value of n tested in the program that resulted in the highest correlation coefficient.

The results presented reveal that considerable variation in kinetic parameters results when TG curves for several samples are analyzed by the computer method of Reich and Stivala. Table 1 shows that the mean values and the sample standard deviations in the activation energies for decomposition of the ammonium salts are virtually identical when determined by either the Reich and Stivala method or the Coats and Redfern method. Selecting an optimum n value for the Coats and Redfern method would have likely made any differences even smaller. The data in Table 2 show that, for the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2\ H_2O$, virtually identical results are obtained whether the analysis is carried out by the Reich and Stivala method or the Coats and Redfern method. A sample giving a high or low n or E value by one method generally gave corresponding values by the other. This is an encouraging confirmation of the two methods. In spite of this, both the extreme spread in activation energy values and the sample standard deviations are virtually identical. The results presented reveal that considerable sample-to-sample variation results when TG data are analyzed by either method. In that sense, there appears to be no advantage to the computer method. It would be convenient if the computer methods reduced somewhat the rather large sample-to-sample variations. Unfortunately, they do not. The fact is that no data analysis method will give reliable kinetic parameters from a single TG curve. Clearly, some consideration of this situation is required for the plethora of kinetic parameters being reported to be properly evaluated and compared. It is also essential when various data analysis methods are being compared [16].

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