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COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XIII

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ABSTRACT

Several procedures have been previously reported whereby non-isothermal TG (NITG) data can be analyzed for values of the activation energy (E) independent of values of the reaction order (n). In this paper, other expressions will be derived for the estimation of E which are essentially independent of n-values and are valid at relatively low degrees of conversion. These equations are applied to NITG data for a siloxane and teflon, as well as for theoretical data. The resulting computer and graphical procedures are both utilized to estimate E-values. Limitations of the methods are also mentioned.

INTRODUCTION

Several procedures have been reported whereby data obtained from non-isothermal TG (NITG) curves can be analyzed to afford values of the activation energy (E) alone without prior knowledge of the reaction order (n) (e.g., refs. 1–9). Thus, multiple heating rates [1–6], maximization of rate [7,8], and areal [9] methods have been employed. In this paper, other expressions will be presented for the estimation of E alone which are independent of n-values. Data were utilized from NITG curves at relatively low degrees of conversion. The resulting equations were applied, by means of a computer, to NITG data for octamethylcyclotetrasiloxane (OMCS), teflon, and to theoretically generated NITG data. Further, graphical procedures were devised to corroborate the results obtained.

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THEORY

For an "n-type" unimolecular (or pseudo-unimolecular) decomposition by means of NITG, we may write (assuming that $1 \gg 2RT/E$)

$$\left[1-(1-\alpha)^{(1-n)}\right]/(1-n)=(ART^2/EB)\exp(-E/RT) \qquad (1)$$

where, α = fractional conversion; A = pre-exponential factor; B = constant rate of heating; T = temperature (K); R = gas constant. (This expression does not apply when n is exactly equal to unity. However, this need not concern us due to the approximations made as well as for other reasons mentioned subsequently.)

At low conversions ($1 \gg \alpha$), eqn. (1) can be converted into

$$\alpha=(ART^2/EB)\exp(-E/RT) \qquad (2)$$

Equation (2) can then be converted into

$$(E/R)=\ln\left[F\,(T_2/T_1)^2\right]\,/\,[(1/T_2)-(1/T_1)] \qquad (3)$$

where, $F=(\alpha_1/\alpha_2)$ and is maintained constant. If we now let $\tau=T_2/T_1$, eqn. (3) becomes

$$(E/RT_1)=\ln(F\tau^2)\,/[(1/\tau)-1] \qquad (4)$$

RESULTS AND DISCUSSION

From eqn. (4), it can be observed that when F is held constant, E/RT_1 may be plotted vs. τ ($=T_2/T_1$). Such plots have been carried out and are depicted in Fig. 1 for values of $F=0.6$, 0.7, 0.8, and 0.9. The various values of F were realized as follows. Smooth plots were initially made of α vs. T utilizing low conversion values (0.01–0.1) from the target NITG data. Then appropriate values of α–T were estimated from the plots, maintaining F constant. In this connection, values of α–T for $F=0.8$ are shown in Table 1 using theoretical NITG data [10]. Values of α–T for $F=0.8$ were also obtained in this manner from NITG data for OMCS and teflon [11].

The α–T data obtained were analyzed for E-values employing three different procedures. In one procedure (P-1), values of T_2/T_1 were estimated for successive data pairs (see Table 1). Then an average value of T_2/T_1 was calculated. From this value and the median temperature value, an average value of E was estimated utilizing Fig. 1. Thus, in Table 1, for theoretical NITG data, an average value of T_2/T_1 of 1.0097 was calculated. Using this value and a median temperature (K) value of 690.0, $\bar{E}$ was estimated as 29.9 kcal mol^{-1} from Fig. 1 (using the $F=0.8$ curve). Another procedure (P-2) involved the calculation of E-values using individual values of T_2/T_1 and T_1, and Fig. 1. An average E-value is then calculated for all the data. In this

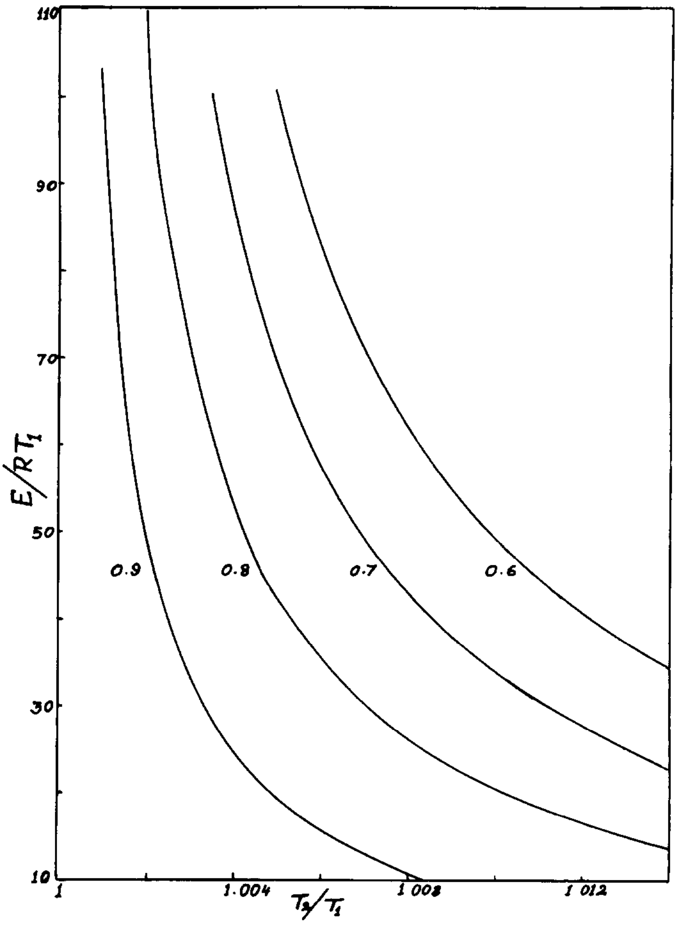

Fig. 1. Plots of E/RT_1 vs. T_2/T_1 at low conversions for various F-values.

manner, for the theoretical data, a value of $\bar{E} = 30.1 \pm 2.3$ kcal mol^{-1} was obtained in excellent agreement with the $\bar{E}$-value obtained using the P-1 procedure. Finally, a computer program was employed (P-3) to estimate values of E/R for all the data using eqn. (3). The P-3 procedure yielded $\bar{E} = 29.6 \pm 2.4$ kcal mol^{-1}, in good agreement with $\bar{E}$-values obtained from procedures P-1 and P-2 (lit. [10], $E = 30$ kcal mol^{-1}, $n = 1$).

The three procedures were then applied to OMCS and teflon ($F = 0.8$). In the case of OMCS, procedures P-1, P-2, and P-3 afforded the following values of $\bar{E}$, respectively: 13.1, 13.4 ± 2.3, and 13.2 ± 2.4 kcal mol^{-1} (lit. [11,12], 11.7 and 12.7 ± 1.5 kcal mol^{-1}). For teflon ($F = 0.8$), the following $\bar{E}$-values were obtained using the three preceding procedures, respectively: 67.7, 69.8 ± 11, and 69.3 ± 11 kcal mol^{-1} (lit. [11], 66–68 kcal mol^{-1}).

It may be noted here that, due to space limitations and in order to maintain clarity, probably not all the curves in Fig. 1 will be useable. Thus, the curves for $F = 0.6$ and 0.7 terminate at E/RT_1-values of 35 and 24,

TABLE 1

Utilization of theoretical values [10] to generate $\alpha - T$ (K) data (for $F = 0.8$) to be analyzed for E-values by both graphical and computer procedures

(T_2/T_1)	T (K)	α	E(kcal mol^{-1}) (from graph)
	726.0	0.1001	
1.0106			28.3
	718.4	0.08008	
1.0104			28.4
	711.0	0.06406	
1.0092			32.4
	704.5	0.05125	
1.0105			27.9
	697.2	0.04100	
1.0104			27.6
	690.0	0.03280	
1.0088			32.8
	684.0	0.02624	
1.0096			29.8
	677.5	0.02099	
1.0104			26.8
	670.5	0.01679	
1.0083			33.9
	665.0	0.01344	
1.0083			33.0
	659.5	0.01075	

respectively. These values may not be low enough for the estimation of relatively low $\bar{E}$-values, as in the case of OMCS (however, if necessary, these curves can readily be extended using eqn. 4). Also, the preceding methods employed are only to a limited extent independent of α- and n-values. Thus, the approximation employed becomes less accurate with increasing values of α and n. From the preceding, it is advisable to utilize values of α not much greater than 0.1 and n-values should not be much above 1.5. It is also obvious that great care should be exercized in estimating T (K)-values at low conversions (maintaining F constant). As mentioned earlier, the approximation used in this paper should still be valid even when $n = 1$ exactly since the resulting expressions become independent of n. Further, even if $n = 1$ exactly, some deviations from this order would be anticipated during the generation of $\alpha - T$ data (keeping F constant). Another consideration, in this regard, is the restriction of the number of significant figures that can be used in practice.

Finally, it may be of interest to mention an application of the P-1 procedure to theoretical NITG data for an Avrami mechanism (A3). In this case, in order to utilize the curve for $F = 0.9$ in Fig. 1, it was necessary that $\alpha_1/\alpha_2 = 0.729$. For seven α-values ranging from 0.016 to 0.11, an average

$T_2/T_1 = 1.0052$ was obtained along with a median $T = 807$ to yield $\bar{E} = 29.5$ kcal mol^{-1} (lit. [10], $E = 30$ kcal mol^{-1}). However, it was necessary to know in advance the type of Avrami mechanism involved.

The P-1 procedure was also applied to NITG data for magnesium hydroxide to test the effect, if any, of an apparent high value of n (ca. 1.5) [13]. For seven α-values ranging from 0.03 to 0.12, an average $T_2/T_1 = 1.0047$ was obtained for a median $T = 628$ to yield $\bar{E} = 56.5$ kcal mol^{-1} ($F = 0.8$ curve in Fig. 1 was used); lit. [13–18], $E = 53$–57 kcal mol^{-1}.

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