STATISTICAL EVALUATION OF NON-ISOTHERMAL DECOMPOSITION KINETICS ANALYSIS METHODS FOR AIBN

C. M. Neag, T. Provder and *R. M. Holsworth*

THE GLIDDEN COMPANY, DWIGHT P. JOYCE RESEARCH CENTER, STRONGSVILLE, OHIO 44136 U.S.A.

Decomposition kinetics parameters were obtained from non-isothermal DSC data for the decomposition of AIBN by two data analysis methods. A statistical evaluation of the results showed that there was no difference between the results obtained by each data analysis method and that the heating rate did not significantly affect the values of the kinetics parameters. Both data analysis methods isolate the order of reaction, n, the activation energy, E, and the Arrhenius factor, A, from a single non-isothermal scan of the decomposition reaction.

A number of techniques have been developed for measuring kinetics constants of chemical reactions from DSC data. The primary advantage of these techniques is their speed and simplicity. In recent years, research efforts in reaction kinetics analysis have centered on differential data analysis methods based on isothermal [1–3], temperature variant or dynamic [4–5], and multiple scan methods [6–7]. Each method uses the rate of heat evolution as the computational parameter, implicitly assuming, among other things, that the reaction is not autocatalytic, has one rate limiting step, and is unaffected by changes in reactant concentration.

Even though much has been written about the theoretical validity and general applicability of non-isothermal reaction kinetics analyses by DSC [8–12], particularly to thermoset cure [13–15], non-isothermal techniques have gained broad acceptance for a variety of uses. Although non-isothermal kinetics analysis techniques are widely accepted, there are remarkably few published analysis which verify the precision and validity of the techniques. While tests of the accuracy and validity of non-isothermal kinetics are generally difficult experimentally, statistical analyses of the run-to-run precision of non-isothermal kinetics analysis are straight forward. In this work we assess the precision of the results obtained by two non-isothermal data analysis methods for the degradation of 2,2′-azobis-(isobutyronitrile) (AIBN).

The order of reaction, n, the activation energy, E, and the Arrhenius constant, A,

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were determined as a function of the rate of heat evolution from non-isothermal DSC data in both differential and integral form. The treatment of the kinetics data in integral form is a new technique based on a Nelder-Mead Simplex minimization procedure [17–18]. The new integral approach was developed to allow the analysis of kinetics data not amenable to analysis with differential kinetics methods.

The kinetics parameters for AIBN decomposition were determined by differential and integral methods at five heating rates. The results obtained by each method, heating rate effects and the precision of the results were all examined statistically.

Decomposition kinetics analysis

Values for n, E and ln A for the decomposition of AIBN were obtained by either a differential method based on the work of Borchardt and Daniels [4, 19] or an integral method based on the work of Koehler and coworkers [20].

Differential method

In the differential method, designated THERM, kinetics parameters are determined directly from the decomposition reaction exotherm, while in the integral approach, designated KINET, kinetics parameters are obtained from normalized fractional conversion curves for the decomposition of AIBN. Both methods yield effective kinetics parameters for the overall decomposition reaction. The same AIBN DSC data were used with both methods to facilitate direct comparisons of the methods.

The working equations used in both data analysis methods stem from the general nth order rate equation,

$$\frac{dF(t, T)}{dt} = K[1 - F(t, T)]^n, \tag{1}$$

where $F(t, T)$ is the fractional extent of conversion ($H(t, T)/\Delta H_0$); K, is the rate constant; t (s), is time; and T (K), is the absolute temperature. The Arrhenius expression gives the temperature dependence of the rate constant,

$$K = A \exp(-E/RT), \tag{2}$$

where A (s^{-1}) is the Arrhenius frequency factor, E (J/mol) the activation energy and R the gas constant (J/mol K).

In THERM, the change in enthalpy with increasing temperature is used to obtain a working expression in terms of observable experimental parameters:

$$\ln \frac{1}{\Delta H_0} \frac{dH(t, T)}{dt} = \ln A - \frac{E}{RT} + n \ln \frac{\Delta H_0 - H(t, T)}{\Delta H_0},$$ (3)

where ΔH_0 (J/g) is the total heat of reaction, $H(t, T)$ (J/g) is the partial heat of reaction, and $dH(T, t)/dt$ (J/g $-$ s) describes the change in the sample enthalpy as the reaction proceeds. Equation (3) has a form suitable for multiple regression analysis:

$$Z = a + bx + cy,$$ (4)

where $a = \ln A$, $b = -E/R$, and $c = n$. The reaction kinetics parameters n, E and $\ln A$ are obtained simultaneously from this expression using a non-linear multiple regression analysis. A detailed description of the multiple regression analysis is given elsewhere [16, 19].

Integral method

Normalized fractional extent of conversion data required for the numerical analysis procedure KINET has the form,

$$F(t, T) = 1 - [(n-1) \int_0^t K(T)\, dt + 1]^{1/1 - n}$$ (5)

Equation (5) is solved using a Nelder–Mead Simplex minimization procedure [17, 18] in conjunction with Gauss–Legendre integration. A unique objective function is utilized in the numerical procedure to solve for the kinetic parameters n and E simultaneously. The value for $\ln A$ is then determined from an algebraic expression. A detailed description of the numerical analysis procedure is provided elsewhere [20].

Experimental

AIBN (VAZO 64, DuPont & Co., Bell, W.V.) was recrystallized twice from methyl ethyl ketone (MEK), dissolved in di-N-butyl phthalate (DNBT) (Eastman Chemicals, Rochester, NY.) (0.105 M) and refrigerated at 3°. Samples of the solution were stored in a freezer at $-15°$ and used within two weeks of preparation. Samples of the AIBN/DNBT solution were allowed to equilibrate (about one hour) at room temperature prior to use.

The raw data for each AIBN decomposition analysis was obtained from a DuPont 990/910 DSC thermal analysis system under a 50 ml/min dry nitrogen purge. Data was collected for the decomposition of 5.0 $(+/-0.1)$ mg AIBN samples in open pans. More than 95% of the exotherm marking AIBN

decomposition was used in each kinetics method. Values for n, E and $\ln A$ were determined by the techniques described above using a previously described automated data analysis system [21].

Results and discussion

Validity

The values of n for E and $\ln A$ obtained using KINET and THERM were in excellent agreement with kinetics constants obtained for AIBN decomposition by classical techniques. The results shown in Table 1 reveal that E and $\ln A$ ($n=1$, assumed) from Van Hook and Tobolsky's paper [22] using classical techniques are within a few percent of the results obtained by KINET and THERM. Kinetics parameters obtained with the latter treatments were somewhat higher than those obtained from ASTM method E–698, a multiple scan technique.

Table 1 Thermal decomposition kinetics of AIBN by DSC methods and classical techniques

Method	n	E, J/mol	$\ln A$, s^{-1}
Van Hook/Tobolsky**	(1.00)	128.8	35.0
KINET*	1.02	121.3	33.2
THERM*	1.03	117.9	32.5
ASTM E–698**	(1.00)	99.7	30.5

* mean values for 8 runs, 5 deg/min
** n assumed $= 1$.

Precision

The results obtained by both data analysis methods were closely reproducible. The normalized DSC results typically used for each kinetics treatment are shown in Figure 1. Figure 2 illustrates the fit between experimental data and a linear regression line obtained with the differential method while Figure 3 illustrates the typical agreement between the experimental and calculated conversion for data obtained using the integral method. Data for replicate runs at 5 deg/minute and 20 deg/minute are shown in Table 2. Statistical analysis of the results in Table 2 reveals excellent reproducibility in both the differential and integral kinetics treatments. Standard deviations (s) range from 3% to 9% of the mean value, depending on the kinetics parameter, while correlation coefficients determined for Arrhenius plots averaged 0.9974 ($+/-0.0023$) for eight runs at 5 deg/min and 0.9982 ($+/-0.0016$) for 5 runs at 20 deg/minute.
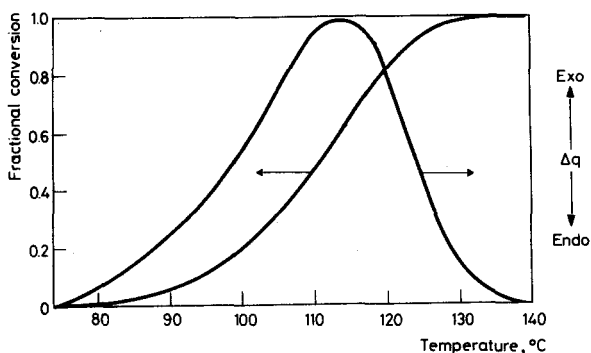
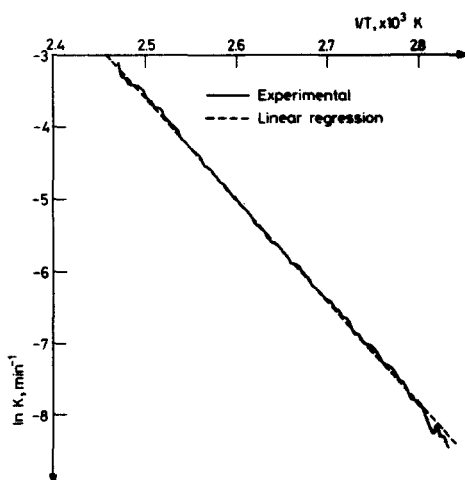**Fig. 1** Normalized DSC data in differential and integral form

Fig. 2 Arrhenius plots for kinetics parameters determined from DSC data and a linear regression line over the temperature range selected for kinetics evaluation. ———— Experimental. – – – – Linear regression

Variation between results from differential and integral treatments

The values of n, E, and $\ln A$ obtained from KINET and THERM are in excellent agreement and statistically equivalent. The kinetics parameters obtained by KINET and THERM were compared statistically two ways: paired-sample t-tests (or student-t) and one way analysis of variance (ANOVA). The t statistic compares the means of each sample population. When the difference between sample means is large, then the corresponding t values also are large and the difference between the
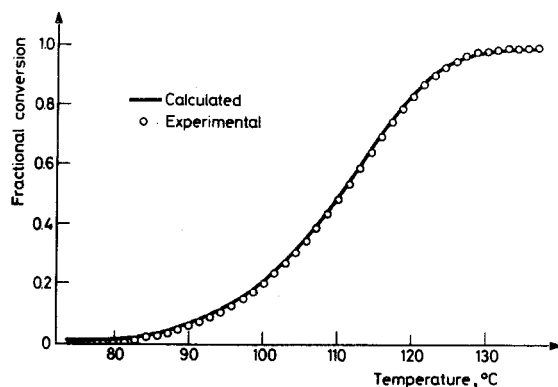
Fig. 3 Plot of experimental and calculated (KINET) fractional conversion for AIBN decomposition. —
—— Calculated. ○ ○ ○ Experimental

Table 2 Comparison of the thermal decomposition of AIBN kinetics parameters determined with KINET and THERM at two heating rates

		5 deg/min				
		KINET			THERM	
Rep	*n*	*E*, J/mol	ln *A*, s^{-1}	*n*	*E*, J/mol	ln *A*, s^{-1}
1	0.97	117.1	31.6	0.96	112.1	30.1
2	1.02	117.5	31.8	1.02	117.5	31.8
3	1.06	143.0	39.9	1.05	136.7	37.9
4	1.07	120.0	32.6	1.06	119.6	32.5
5	1.00	122.5	23.3	1.04	122.1	23.2
6	1.02	116.7	31.5	1.04	116.7	31.5
7	0.98	115.0	31.0	0.98	113.7	30.5
8	1.05	120.0	32.5	1.05	119.2	32.3
Mean	1.02	121.3	33.2	1.03	119.6	32.5
s	0.04	9.2	2.9	0.04	7.5	2.4
		20 deg/min				
		KINET			THERM	
Rep	*n*	*E*, J/mol	ln *A*, s^{-1}	*n*	*E*, J/mol	ln *A*, s^{-1}
1	1.03	127.1	34.7	1.04	123.8	33.6
2	0.98	125.0	34.3	0.98	116.7	31.6
3	0.98	110.1	29.7	1.01	111.2	29.8
4	0.94	113.3	30.4	0.98	113.7	30.6
5	0.98	127.9	34.9	1.07	125.0	34.1
Mean	0.98	120.8	32.8	1.02	117.9	31.9
s	0.03	7.9	2.5	0.04	6.3	1.9

(Rep = replicate scan, *s* = standard deviation).

groups is statistically significant. The other statistical measure, one-way ANOVA, compares within group variation with between-group variation. When the variance between sample data from each group is large in comparison to variance within each group, F values will be large and there will be a statistically significant difference in the variability of the two samples.

The results for the paired t-test shown in Table 3 indicate that there is no significant difference in the sample means obtained with KINET and THERM. Table 3 includes t values and the probability ($p = 0.05$) that the observed difference between sample means would have occured by chance alone. The observed difference in sample means for each kinetics method would have been significant if $t > 2.365$ for results at 5 deg/min and $t > 2.776$ for results at 20 deg/min.

Table 3 Results for paired t-test and analysis of variance (ANOVA) for n, E, and ln A for AIBN decomposition at 5 deg/min and 20 deg/min

	N	n	s	E, J/mol	s	ln A	s
KINET	8	1.021	0.036	121.3	9.2	33.2	2.9
THERM	5	1.025	0.040	119.6	7.5	32.5	2.5
ANOVA	$F =$	0.063		0.177		0.066	
T-test	$t =$	0.82		2.04		1.98	

Critical t values: $t = 2.365$ ℮ 5 deg/min & 2.776 ℮ 20 deg/min ($p = 0.05$); $df = 7$ at 5° & $df = 4$ at 20°.

Critical F value: 4.6 ($p = 0.05$); $df 1 = 1$, $df 2 = 8$; $s =$ std. dev. ($n-1$).

There was no significant difference in the results generated by ANOVA for multiple runs at 5 and 20 deg per minute. F values from the ANOVA shown in Table 3 were well below the value required to show a statistically significant difference ($F = 4.6$, $p = 0.05$) between the differential and integral treatments.

Heating rate effects

Statistical analysis of a series of runs at 5 heating rates reveals that changing the heating rate from 2 deg/min to 20 deg/min does not lead to appreciable differences in the values determined for n, E, and ln A.

This contradicts results obtained by Barrett [23] which revealed that both activation energy and the frequency factor for AIBN decomposition increased with increasing heating rate. The discrepancy between the results described here and those obtained by Barrett may stem from one of several experimental variables, e.g. differences in sample mass, that can influence the results [14].

The kinetics parameters obtained at each of the 5 heating rates shown in Table 4

Table 4 AIBN decomposition kinetics parameters at various heating rates

	KINET			THERM		
Rate, deg/min	n	E, J/mol	$\ln A$, s^{-1}	n	E, J/mol	$\ln A$, s^{-1}
2	1.01	128.8	35.5	1.00	129.2	35.6
5	1.00	121.7	33.1	0.97	117.1	31.6
10	0.97	108.3	35.6	0.93	108.7	29.0
15	1.01	112.9	30.3	0.93	110.8	29.1
20	1.05	126.3	34.4	1.03	127.1	34.7
Mean	1.01	119.6	33.8	0.97	118.7	32.1
s	0.03	8.8	2.2	0.04	9.2	3.0

appear to be in good agreement. The Arrhenius plots obtained using the differential kinetic analysis of data at five heating rates are illustrated in Figure 4. Regression analysis of these plots yields a mean correlation coefficient of better than 0.999. Heating rate effects also were evaluated by comparing kinetics parameters obtained from multiple runs at 5 deg and 20 deg per minute. As in the comparison of KINET and THERM, t-tests were used to assess statistical differences in the kinetics constants obtained at each heating rate. The results of a two sample t-test shown in Table 5 indicate that there are no significant differences in the average values of n, E and $\ln A$ at heating rates of 5 deg/min and 20 deg/min, regardless of the kinetics
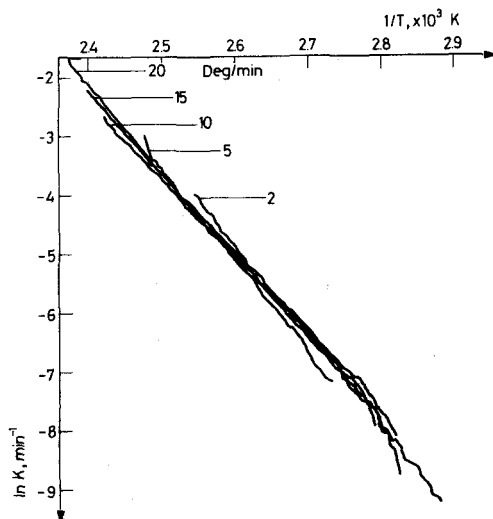
Fig. 4 Arrhenius plots for kinetics parameters determined from DSC data at 2, 5, 10, 15 and 20 deg/minute

Table 5 Comparison of mean values for kinetics parameters obtained at two heating rates

	KINET		
Kinetics parameter	Mean ϱ 5 deg/min	Mean ϱ 20 deg/min	t
n		0.98	1.954
E, J/mol	121.3	120.3	0.120
ln A, s^{-1}	31.8	32.8.	0.467
	THERM		
Kinetics parameter	Mean ϱ 5 deg/min	Mean ϱ 20 deg/min	t
n	1.03	1.02	0.439
E, J/mol	119.6	117.9	0.396
ln A, s^{-1}	31.2	31.9	0.369

critical t value = 2.776 at $p = 0.05$ with d$F = 11$

treatment. In addition, analysis of covariance (BMDP P2V, BMDP Statistical Software, Los Angeles, CA.) revealed that there were no significant rate effects in the results obtained for AIBN decomposition.

Conclusions

The kinetics parameters obtained for the non-isothermal decomposition of AIBN by differential and integral data analysis treatments were found to be statistically equivalent, reproducible within 10% of the mean value. They were also in excellent agreement with kinetics constants obtained with classical techniques, and independent of heating rate.

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Zusammenfassung — Mittels zwei Datenauswertungsmethoden werden aus Ergebnissen von nichtisothermen DSC-Werten kinetische Parameter für die Zersetzung von AIBN ermittelt. Eine statistische Auswertung der Ergebnisse ergab, daß zwischen den durch die beiden Datenauswertungsmethoden erhaltenen Resultaten kein Unterschied besteht und daß die kinetischen Parameter von der Aufheizgeschwindigkeit nicht bedeutend beeinflußt werden. Beide Verfahren liefern auf der Basis eines einzigen, nichtisothermen Durchlaufes der Zersetzungsreaktion die Reaktionsordnung n, die Aktivierungsenergie E und den Arrheniusfaktor A.

Резюме — Полученные с помощью неизотермической ДСК кинетические параметры реакции разложения AIBN обрабатывались двумя методами анализа. Проведенная обоими методами статистическая оценка результатов не показала как различия между ними, так и то, что скорость нагрева не оказывает существенного влияния на значения кинетических параметров. Оба метода анализа, исходя только из одного неизотермического измерения реакции разложения, позволили определить порядок реакции (n), энергию активации (E) и аррениусовский множитель (A).