



Interlaboratory Kinetics Studies Using ASTM International Standards E2041 and E698 and Trityl Azide

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ABSTRACT

ASTM International standards E2041 and E698 are commonly used to determine kinetic parameters for thermally unstable materials using differential scanning calorimetry (DSC). E2041 employs the single scan Borchardt and Daniels approach while E698 uses the Ozawa/Flynn/Wall multiple heating rate method. These approaches are applicable to n th order reactions. E2041 determines the kinetic parameters of activation energy, pre-exponential factor and reaction order while E698 assumes first order. Two interlaboratory tests were conducted using trityl azide to evaluate the precision of these two methods. The within laboratory activation energy relative standard deviation of the two methods is approximately equal at 3.0 %. However, E698 shows a between laboratory reproducibility relative standard deviation of 6.5 %, more than a factor of 2 better than the value of 14 % for E2041.

INTRODUCTION

Trityl azide (also known as azidotriphenylmethane) was suggested nearly 25 years ago by Jim McCarty and Allan Duswalt as a reference material for evaluation of kinetic parameters (1). They proposed this well-behaved, room temperature stable material with first order decomposition kinetics for the evaluation of ASTM International standard E698 then in development (2). Since that time it has been widely used by TA Instruments and others as a demonstration tool for n th order kinetic software programs.

Since the early 1970's, ASTM International has developed a series of kinetic methods using differential scanning calorimetry to meet a variety of needs. These include E2041 (3), which makes use of a single scan using the Borchardt and Daniels approach (4), E698 using the multiple heating rates Ozawa (5) and Flynn and Wall (6) approach, and E 2070 (7) using the isothermal Sestak-Berggren approach (8).

One of the features of ASTM International standards is the inclusion of a precision and bias information. The data for this section is derived from interlaboratory tests using real-world samples to estimate the within laboratory repeatability and the between laboratory reproducibility. The availability of validated precision and bias information aids the user to ascertain whether a particular method will meet the application needs at hand.

This paper reports on the recently completed interlaboratory tests (ILTs) for E2041 and E698. In both cases trityl azide is used as the test specimen enabling the results of the two studies to be compared.

EXPERIMENTAL

The trityl azide used in these ILTs was obtained from Pfaltz and Bauer (Waterbury, CT) and is supplied as 95 % purity powder. The thermogravimetric decomposition profile and DSC thermal curve for the specimen are shown in Figure 1 as their overlay. The DSC profile (at the bottom) shows a melting endotherm near 60.3°C and a smooth continuous exothermic decomposition peaking near 230°C. The TGA weight loss profile (at the top) is also smooth and continuous although the first derivative (in the middle) appears to have a slight low temperature shoulder.

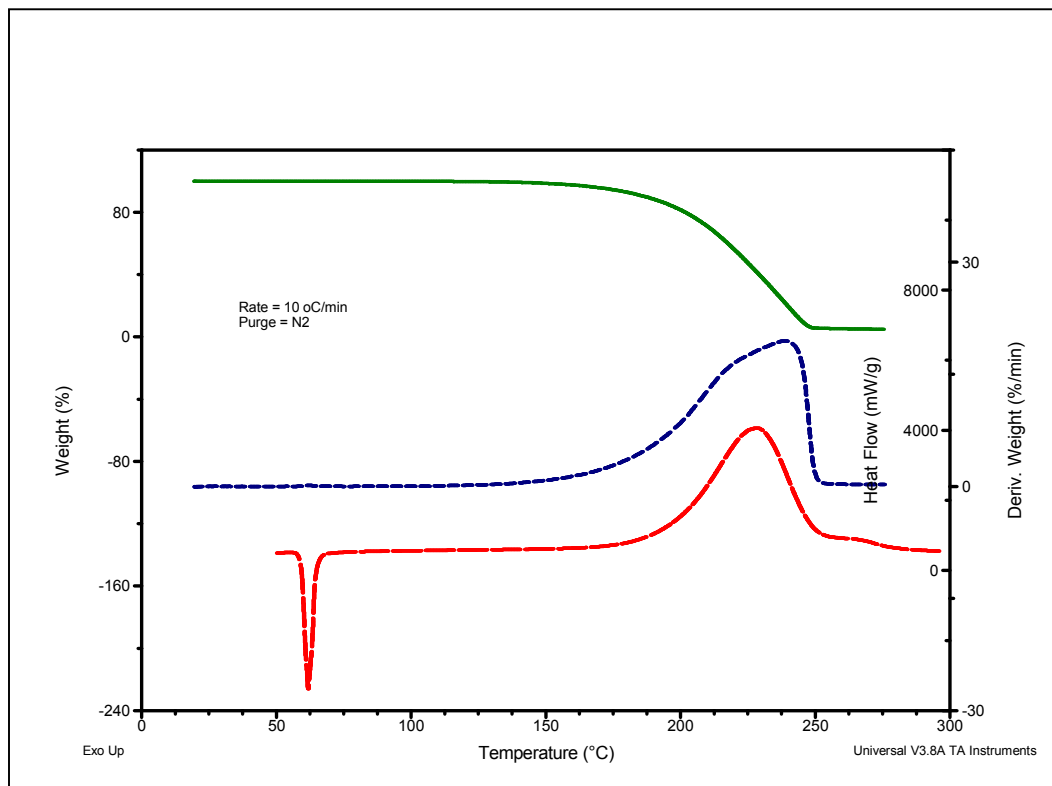


Figure 1 - TGA, Derivative TGA and DSC Profiles for Trityl Azide

Interlaboratory test packages for each method were sent to 15 volunteer laboratories. Results received are identified in Table 1 for the E2041 Borchardt and Daniels method. For the E698 Ozawa/Flynn/Wall approach, the 10 laboratories illustrated in Table 2 supplied results. (The author wishes to express thanks to all of the participants without whose effort this work would not be possible.) For E2041, each laboratory was asked to determine activation energy, logarithm of the pre-exponential factor and reaction order in a series of 5 replicates. For E698, the participants were asked to perform the determination at a series of 5 different heating rates.

WORKER	AFFILIATION	LOCATION
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Ramon Artiaga	Univ. de Coruna	Ferrol, PS
Bob Behme	Science Resources	Evansville, IN
Roger Blaine	TA Instruments	New Castle, DE
Bruce Cassel	TA Instruments	Brookfield, CT
Robert Fouchard	Canadian Explos. Res.	Ottawa, ON
Tom Gallagher	Akzo Nobel	Dobbs Ferry, NY
Laura Littlejohn	Ashland Spec. Chem.	Dublin, OH
Coleen McFarland	Polymer Diagnostics	Avon Lake, OH
Steffen Neuenfeld	Merck	Damstadt, GR
Stephane Ruelle	CONDAT	Chasse Sur Rhone, FR
Steve Sauerbrunn	Mettler-Toledo	Newark, DE
Daniel Sorenson	Naval Surf. Warfare Ctr	Indian Head, MD
Albert Tse	PPG Industries	Monroeville, PA
Mauro Zarrelli	CIRA	Caserta, IT

Table 1 - Participating Laboratories in E 2041 Borchardt and Daniels Interlaboratory Test.

WORKER	AFFILIATION	LOCATION
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Bob Behme	Science Resources	Evansville, IN
Dale Cheetham	Lilly Research	Indianapolis, IN
E. Robert Fretz	Corning	Corning, NY
Robert Fouchard	Canadian Explos. Res.	Ottawa, ON
John Jones	Astra Scientific	Pleasanton, CA
Tom Ramotowski	Naval Undersea War. Ctr.	Newport, RI
Tom Sanders	Dow Corning	Midland, MI
Albert Tse	PPG Industries	Monroeville, PA
Curtis Teague	Eastman Chemical	Kingsport, TN
Guy Van Assche	Vrije Universiteit Brussel	Brussel, BE

Table 2 - Participants in the E 698 Ozawa/Flynn/Wall Interlaboratory Test

RESULTS AND DISCUSSION

In any interlaboratory test, the results must be carefully examined, both statistically and with common sense, to provide results that a user of the data may find understandable and useful. This typically means “filtering out” results that were not run according to the experimental protocol and data that are outliers from those received by other laboratories. In all cases, some effort must be exerted to try to locate the sources of the discrepancy.

For E2041, data was received from 15 laboratories (one participant submitted two sets of results) and were statistically treated by ASTM International standard E691 (9). One laboratory was found to be a between-laboratory k outlier for activation energy, pre-exponential factor and reaction order. An attempt was made to work with the author to uncover the potential source of difficulty without success. The results of this laboratory were excluded from further consideration.

The results for a second laboratory were found to be a within-laboratory outlier for activation energy and between-laboratory k outlier for logarithm of the pre-exponential factor. For activation energy, the one outlying value was replaced by the mean value for the remaining four results (as is permitted by E 691). The results of the same laboratory were discarded for logarithm of the pre-exponential factor and reaction order.

The results of a third laboratory were found to be a between laboratory k outlier for the logarithm of the pre-exponential factor. It was found that the laboratory did not follow the experimental protocol the value of reaction order but rather fixed the value at 1.00. Thus the activation energy results were retained and the logarithm of the pre-exponential factor (which depends upon reaction order) and reaction order results were discarded.

PROPERTY	ACTIVATION ENERGY (kJ/Mol)	Log [PRE-EXPON. FACTOR (Ln (1/min))	REACTION ORDER
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Mean	165.1	17.2	1.32
Repeat. Std. Dev.	4.98	0.577	0.087
Repeat. Rel. Std. Dev.	3.02 %	3.35 %	6.58 %
Repro. Std. Dev.	16.2	1.69	0.293
Repro. Rel. Std. Dev.	14 %	12 %	22 %
Number	14	12	13

Table 3 - Interlaboratory test results for E2041 Borchardt and Daniels kinetics

The results for the remaining 14 laboratories for activation energy, 12 laboratories for logarithm of the pre-exponential factor and 13 laboratories for the reaction order are presented in Table 3.

For E698 Ozawa/Flynn/Wall kinetics, a total of 10 laboratories reported results for activation energy and logarithm of the pre-exponential factor. (The reaction order is assumed to be 1.0 in the Ozawa/Flynn/Wall approach.) The mean value and standard deviation for activation energy results were determined using E1970 (10). The results for two laboratories were found to be outliers at the 95 % confidence level. These results were discarded. The mean value and standard deviation for activation energy and logarithm of the pre-exponential factor were determined for the remaining 8 laboratories and are presented in Table 4.

The relative standard deviation of activation energy is obtained from the best-fit straight-line slope used to determine the activation energy. The relative standard deviation values obtained from each laboratory were “pooled” according to E1970 are presented in Table 4. The relative standard deviation of the logarithm of the pre-exponential factor was calculated from the propagation of uncertainties (11) and is also presented in Table 4.

PROPERTY	ACTIVATION ENERGY (kJ/Mol)	Log [PRE-EXPON. FACTOR (Ln (1/min))	REACTION ORDER
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Mean	145.5	15.2	1.00
Repeat. Std. Dev.	3.74	0.62	
Repeat. Rel. Std. Dev.	2.58 %	4.09 %	
Repro. Std. Dev.	9.41	1.28	
Repro. Rel. Std. Dev.	6.47 %	8.44 %	
Number	8	8	

Table 4 - Precision for E698 Ozawa/Flynn/Wall Kinetics

DISCUSSION

The within laboratory activation energy relative standard deviations for E2041 and E698 are 3.0 and 2.6 % and are indistinguishable according the statistical F-test. The between laboratory activation energy relative standard deviations were 14 and 6.5 %, respectively. This indicates that the within laboratory precision for the two methods is comparable but that E698 is substantial more reproducible from one laboratory to the next.

The mean values for activation energy were found to be 165 kJ/mol for E2041 and 146 kJ/mol for E698. The logarithm of the pre-exponential factors was 17.2 and 15.2, respectively with the pre-exponential factor expressed as min^{-1} . The Borchardt and Daniels approach determined the reaction order to be 1.32 while the Ozawa/Flynn/Wall approach assumes the value to be unity. The activation energy values are within two

standard deviations of each other, and they are statistically dissimilar at the 95 % confidence level. Similarly the logarithm of the pre-exponential factor and the reaction order are within two standard deviations of each other, but as they are related, no significance is attributable to their similarity or difference.

SUMMARY

The DSC kinetic approach of E698 Ozawa/Flynn/Wall and E2041 Borchard and Daniels were found to provide comparable values for activation energy, logarithm of the pre-exponential factor and reaction order. The within laboratory precision for the two methods are also similar. However, E698 Ozawa/Flynn/Wall method showed between laboratory reproducibility that was better by a factor of 2 from that of E2041 Borchardt and Daniels. In contrast, the time required to obtain results using the E2041 Borchardt and Daniels approach is on the order of 1 hour while that for the E698 Ozawa/Flynn/Wall method is about one day.

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KEYWORDS

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