Journal of Thermal Analysis, Vol. 49 (1997) 1653-1660

SMALL SCALE ADIABATIC DEWAR TECHNIQUES TO DETERMINE EXOTHERMIC ONSET TEMPERATURES

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Abstract

The heightened focus on safety in the chemical process industry has resulted in a growing trend to provide reliable thermochemical information before process scale-up. The exothermic onset temperature of compounds is of key concern. The small scale adiabatic dewar age (SSAD) test, developed at Merck Research laboratories, is used to determine exothermic onset temperatures. These tests are conducted under nearly adiabatic conditions using specially designed dewar sample cells and commercially available programmable calorimeters. The dewar cell method offers a rapid and accurate method to enhance standard test procedures and allows measurement of auto catalytic behavior using small samples.

The SSAD technique is applicable to both solids and liquids and has the following advantages: 1) small sample size, 2) ability to handle compounds in which exothermic activity is accompanied by large pressure increases without damaging experimental equipment, 3) accurate determination of exothermic onset temperature, 4) ease of experiment set-up, 5) ease of data interpretation and 6) rapid experimental turn around time.

The determination of the exothermic onset temperature using the SSAD technique will be presented and compared to data obtained using standard and isothermal age techniques.

Keywords: adiabatic dewar, exothermic onset temperature, safety, small scale

Introduction

The small scale adiabatic dewar (SSAD) test was developed to provide reliable information as to exothermic onset temperatures using small quantities of test material. Large quantities of materials are often unavailable during the early stages of pharmaceutical process development.

Typically, adiabatic dewar ages and/or ARC® (accelerated rate calorimetry) studies are used in determining exothermic onset temperatures. These tests use relatively large amounts of sample compared to the SSAD and are time consuming to run. The SSAD technique is a novel calorimetry technique which has been developed for use with the ASI Radex [1] and Fauske RSST [2] calorimetry instruments, using specially designed Merck dewars [3]. The Merck dewar provides reasonably accurate exothermic onset temperatures utilizing small samples (~1 g). SSAD technique employs a reusable glass dewar cell [4]. The sample is held under adiabatic conditions at a preset temperature for an extended period of time, usually ~12 h, with the aged sample being reevaluated for any change in the size of the original

0368–4466/97/ $ 5.00

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exotherm (ΔH). A decrease in the size of the original exotherm indicates heat was evolved during the age, and thus the exotherm initiated during the age. In addition, any auto-catalytic behavior may be detected. The results must be further evaluated via RSST, VSP or other suitable methodology in order to determine the potential consequences of exotherm initiation during chemical processing.

The determination of decomposition onset temperatures for dicumyl peroxide and two proprietary compounds using the Small Scale Adiabatic Dewar technique are presented. A comparison is made between decomposition temperatures determined using both dewar and non-dewar cells. In addition, the data obtained in this study for dicumyl peroxide are compared to the data obtained in a DIERS Users Group Phase VII Round Robin Test [5] for dicumyl peroxide.

Experimental

Three different test systems/methods utilizing three different test cells as follows:

1) Fauske RSST with standard glass and Merck designed dewar cell [3]
2) ASI Radex with standard glass and Merck designed dewar cell [3]
3) adiabatic calorimetry with standard dewar cell and a specially designed temperature controlled oven
4) TA 2200 DSC [6] and the Merck reusable metal crucible [7].

These systems were used to determine the exothermic onset temperatures for three compounds. Two different heat profile programs were used; a temperature scan utilizing a constant heat-up rate and an age technique using a set temperature.

Experimental technipue

Step 1

A temperature scan from ambient to ~300°C at 2°C min^{-1} is run on each sample using the four experimental test systems. The results of these are evaluated and the lowest exothermic onset temperature is used for the first adiabatic age.

Step 2

An adiabatic age, at the exothermic onset temperature determined in Step 1, is run for ~12 h in each of the test cells used in Step 1. In the RSST, Radex and Merck designed dewar cells the sample is compacted by lightly tapping the cell. The typical quantity used in the RSST is ~5 g for a solid and ~8 ml for a liquid sample. Radex cells use ~1 g for solids and ~5 ml for a liquid. The weights used will vary somewhat depending upon the density of the sample used.

Step 3

A DSC scan at 2°C min^{-1}, using the Merck metal crucible, is run on the aged sample from Step 2. The size of the resulting exotherm (ΔH) is compared to the

original exotherm in the unaged sample. The cell base, Merck metal crucible, sample weight and heat up rate are identical to that used to determine the exotherm size (ΔH) of the unaged sample (Step 1). A decrease in the size of the exotherm (ΔH) indicates heat evolution during the age, and therefore, the exotherm initiated during the age. When using liquids for the age period, the sample must be carefully weighed both before and afterwards. When calculating the size of the exotherm after the age period any weight loss is compensated.

To provide for accurate results, a total of 3 to 5 scanning DSC runs must be performed on the unaged and aged samples. The start and end points for the exotherms, both before and after the ages, must be carefully evaluated and selected using a sigmoidal curve in the analysis of the size of the exotherm.

Step 4

Steps 2 and 3 are repeated at lower temperatures in ~5°C increments until no change in the size of the exotherm is observed for the aged sample.

Calibration of the small scale adiabatic dewar system

The SSAD technique was calibrated using solid dicumyl peroxide and a 40% (wt.%) solution of dicumyl peroxide in ethyl benzene. A Round Robin testing program, sponsored by the DIERS Users Group, identified the onset temperature for the decomposition for a 40% by weight solution of dicumyl peroxide in ethyl benzene using standard DSC, ARC®, RSST and VSP test cells and procedures.

In the first step of the SSAD calibration, the decomposition onset temperatures for both the solid and ethyl benzene solution of dicumyl peroxide were determined using the experimental test systems. The results are compared with the DIERS Round-Robin test and are presented in Table 1.

In the second stage of the calibration, both the solid and liquid samples were aged adiabatically using Merck designed dewar cells in a Fauske RSST unit and an

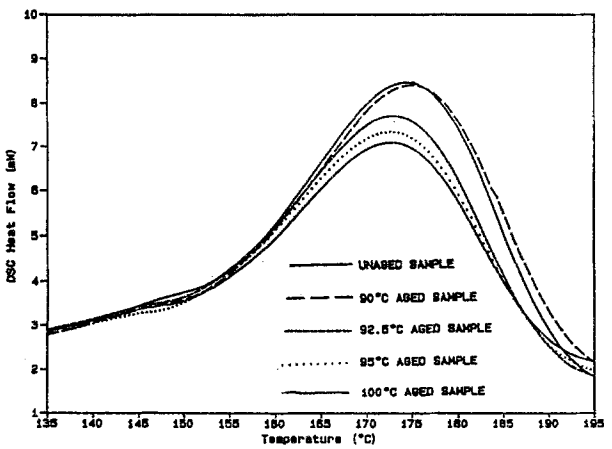

Fig. 1 DSC runs of unaged dicumyl peroxide *vs.* SSIA DSC aged samples (in ethyl benzene)

Table 1 Comparison of exotherm onset temperatures for dicumyl peroxide solid and 40% weight in ethyl benzene (Temperature scan mode)

Results from	Instrument	Cell	T_{onset}/°C	
			solid	EtBz solution
Diers Round-Robin[1]	DSC	Stainless steel test cell	test not run	109.4 to 159.2 (avg 150±6.1°C)
SSAD calibration	DSC	Hastelloy B crucible[7]	125	124
Diers Round-Robin[1]	RADEX	glass cell	not available	not available
SSAD calibration	RADEX	glass cell	112	117
Diers Round-Robin[5]	RSST	glass cell	notavailable	110 to 115 (avg 115.2±4.1°C)
SSAD calibration	RSST	glass cell	112.5	118
Diers Round-Robin[5]	ARC	regular test cell	not available	97 to 107 (avg 103.4±3.2°C)
SSAD calibration	RADEX	special radex Dewar cell[3]	103	105
SSAD calibration	RSST	special RSST Dewar cell[3]	104	103
SSAD calibration	adiabatic Dewar oven	standard Dewar	104	test not run[a]

(a) System can not be sealed to prevent solvent loss.

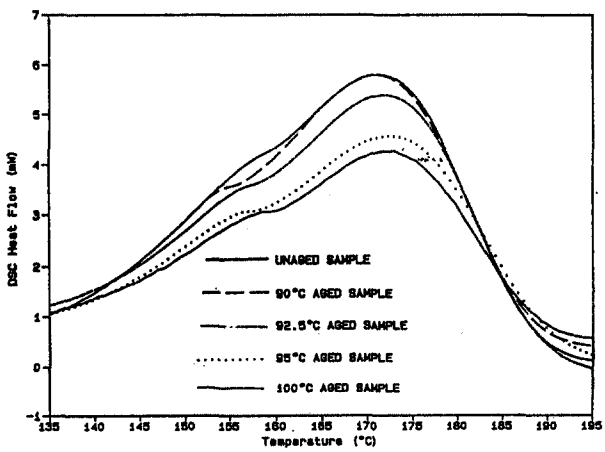

Fig. 2 DSC runs of unaged dicumyl peroxide *vs.* SSIA DSC aged samples (solid)

ASI Radex unit. The predetermined age temperatures used were 90, 95 and 100°C, as per Step 2 of the experimental technique section. The aged samples were then re-

run, as per Step 3 of the experimental technique section, in a Hastelloy B metal crucible and compared to that of the unaged sample to determine if decomposition had occurred. A decrease in the size of the original exotherm (ΔH) in the dicumyl peroxide indicates that heat was evolved and, therefore, decomposition initiated during the age. See Figs 1 and 2 for a comparison of the DSC reruns of the isothermal aged solid and ethyl benzene solution of dicumyl peroxide.

Case studies

Results for two Merck proprietary compounds using the SSAD technique are compared to those determined using standard adiabatic dewar, RSST dewar and Radex dewar studies.

As per Step 1 of the experimental technique section, the decomposition onset temperature for both proprietary compounds were determined using the experimental test systems and the results are presented in Tables 3 and 4.

Both proprietary compounds were adiabatically aged in the RSST and Radex Merck designed dewar cells at three predetermined temperatures, as per Step 2 of the experimental technique section. The aged samples were then rerun, as per

Table 2 SSAD determination of exothermic onset temperature for dicumyl peroxide solid and 40% weight in ethyl benzene (Adiabatic temperature age mode)

Instrument	t_{aged}/ h	T_{age}/ °C	Decomposition / %	
			exo, in solid	exo in EtBz
RADEX	12	90	0	0
RSST	12	90	0	0
RADEX	12	95	-10.2	-9.4
RSST	12	95	-9.6	-10.3
RADEX	12	100	-13.3	-14.6
RSST	12	100	-14.9	-13.4

Table 3 Comparison of exotherm onset temperatures for proprietary compound 1 (Temperature scanning mode)

Instrument	Type of cell	T_{onset}/°C		
		Exo $1_{(premelt)}$	Exo 2	Exo 3
RADEX	glass cell	none	109.2	179.9
RADEX	Dewar cell	58.7	108.6	173.4
RSST	glass cell	none	108.3	178.1
RSST	Dewar cell	58.3	108.6	173.4
Adiabatic Dewar oven	standard Dewar	51.4	108.3	175.0

Table 4 Comparison of exotherm onset temperatures for proprietary compound 2 (Temperature scanning mode)

Instrument	Type of cell	T_{onset}/°C	
		exo $1_{(premelt)}$	exo 2
RADEX	glass cell	72.5	125.5
RADEX	Dewar cell	57.6	124.5
RSST	glass cell	66.8	125.0
RSST	Dewar cell	51.5	120.5
Adiabatic Dewar oven	standard Dewar	48.3	125.0

Table 5 SSAD determination of exotherm onset temperatures for proprietary compound 1 (Adiabatic temperature age mode)

Instrument	t_{aged}/h	T_{age}/°C	% change in ΔH
RADEX	12	35	0
RSST	12	35	0
RADEX	12	40	-6.63
RSST	12	40	-5.23
RADEX	12	50	-16.34
RSST	12	50	-16.60

Table 6 SSAD determination of exotherm onset temperatures for proprietary compound 2 (Adiabatic temperature age mode)

Instrument	t_{aged}/h	T_{age}/°C	% change in ΔH
RADEX	12	35	0
RSST	12	35	0
RADEX	12	45	-1.74
RADEX	12	55	-3.06
RSST	12	55	-2.82
RADEX	12	65	-3.89
RSST	12	65	-4.98

Step 3 of the experimental technique section, in a Hastelloy B metal crucible and compared to that of the unaged sample to determine if decomposition had occurred.

The results are presented in Table 5 and 6.

Results

Calibration

The small scale adiabatic dewar scanning technique determined an exothermic initiation temperature of ~103–104°C for the solid dicumyl peroxide, which is equivalent to the standard dewar test method.

The small scale adiabatic dewar age (SSAD) technique determined a decomposition onset temperature greater than 90°C for both the solid and 40% (by weight) ethyl benzene solution of dicumyl peroxide. The lowest ARC (accelerated rate calorimeter) predicted decomposition onset temperature was 97°C. The adiabatic dewar oven test was not run due to the inability to seal the system.

Case Studies

The small scale adiabatic dewar scanning (SSAD) technique determined decomposition onset temperatures are comparable to those determined using the standard corked dewar technique. RSST and Radex dewar ages both predict a decomposition onset temperature of greater than 35°C for both proprietary compounds. More precise initiation temperature could be determined by doing SSAD ages at temperatures between 35 and 40°C.

The SSAD age technique determined a lower decomposition onset temperature than predicted with standard dewar temperature scan runs, ~6°C less for proprietary compound 1 and ~8°C less for proprietary compound 2.

Sensitivity

Calibration of the SSAD technique using dicumyl peroxide indicates the system has a sensitivity equivalent to the DIERS Round Robin Test ARC studies.

Conclusions

The SSAD systems developed by Merck & Co., Inc. (pat. pend.) for use with the ASI Radex and Fauske RSST units, run in an adiabatic mode, are capable of determining decomposition onset temperatures lower than those obtained using dewar methods (standard dewar, RSST dewar, Radex dewar) tested.

The results of the Case Studies presented indicate the SSAD technique is capable of determining lower decomposition onset temperatures than any of the standard dewar temperature scan methods.

These systems when run in a temperature scanning mode and are capable of determining decomposition onset temperatures comparable to those obtained using standard large scale adiabatic dewar test methods and the ARC® test method.

Finally, it should be noted this methodology is useful for determining decomposition onset temperatures only. The consequences of decomposition initiation must be further evaluated via RSST, VSP or other suitable techniques in order to determine the effects on chemical processing.

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