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EVALUATION OF THERMAL STABILITY. AN OVERVIEW

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ABSTRACT

A systematic application of thermal analytical techniques for the assessment of the thermal stability of a material is emphasized. This approach employs ASTM E-27.02 (Methods of Test) and is illustrated using a sulfur—nitrogen heterocyclic compound model.

INTRODUCTION

The ASTM E-27 Committee defines the hazard potential of a chemical as the degree of susceptibility to ignition or release of energy under varying environmental conditions [1]. The key, therefore, to any hazard assessment is "varying environmental conditions" which must include a complete description of the sample (including quality), as well as a realistic representation of external stimuli. Specific to this manuscript is the stability of a material subjected to thermally induced temperature change, i.e. thermal stability.

Increased current awareness of the thermal instability of materials and their potential for casualty was inspired by efforts in government, industry, and academic and insurance institutions. Since 1967, the American Society for Testing and Materials (ASTM) E-27 Committee on Hazard Potential of Chemicals has pursued "the development and standardization of physical and chemical test methods, nomenclature, and the promotion of knowledge and stimulation of research bearing on the hazard potential of chemicals" [1]. More specific are the efforts in thermal stability testing of the E-27.02 subcommittee whose thermal analytical procedures or proposals are included in the methods discussed below.

Governmental concerns for thermal stability are focused in the generation of a classification of "thermally unstable materials" by the Environmental Protection Agency and the Department of Transportation. This classification is designed to be distinct from those of Flammable and Explosive materials classifications. To date, neither government organization has, however, established any test methods to evaluate candidates for this materials classification.

Because even the introduction of heat (temperature change) may be accomplished in numerous ways, a systematic approach to assessing the

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thermal stability of a material is necessary. The text to follow will introduce in brief detail a series of computational and experimental procedures which may be applied sequentially to establish the extent of a material's thermal stability. Analysis of a sulfur—nitrogen heterocyclic compound is included for exemplary purposes.

DISCUSSION

Foremost to a discussion of thermal stability is the criterion which establishes instability. By definition, a material is thermally unstable if it exhibits an exothermic transition. The occurrence of an exothermic transition is observed using the thermal analytical techniques given in Table 1. The basic interrelationships of these procedures may be seen in the evaluation flow chart of Fig. 1.

The experimental classification of an ever increasing list of materials for their thermal stability is an unrealistic undertaking. However, an initial computational screening to establish experimental priorities is possible with a technique such as CHETAH [2]. This computer program utilizes gas phase thermodynamic parameters of the basic functional groups in a material to calculate the maximum potential energy release. A sample computation for the *S,N*-heterocycle is given as Table 2. Experience predicts that materials with a Criterion 1 (ΔH reaction) value more negative than -0.7 kcal g^{-1} may be thermally unstable and require immediate attention. Similarly, for those materials whose ΔH reaction value is more positive than -0.4 kcal g^{-1}, a thermally unstable condition is not likely.

For a material such as our sample compound, where experimentation is necessary, initial examination is accomplished by differential thermal methods (DSC or DTA) for the detection of an exothermic transition [3]. Observance of an exotherm such as in Fig. 2 establishes a tentative "thermally unstable" classification which must be further evaluated.

In addition to the qualitative application, differential thermal methods are also used quantitatively to determine the enthalpy of transition [4], specific heat [5], and the reaction kinetics. One particular kinetics determination is based upon the methods of Ozawa as illustrated in Table 3 [6].

For certain materials, especially volatile nitro and borate compounds, no exothermic transition is observed but thermal instability is anticipated from

TABLE 1

Experimental techniques for thermal stability classification

Technique	Condition of interest
Differential thermal methods (DSC, DTA)	Presence of exotherm
Constant temperature stability (CTS)	No exotherm for 2 h
Heating under confinement	Temperature and pressure change
Adiabatic calorimetry including ARC	Time to maximum rate
Large scale holding tests including SADT	Thermal mass effects

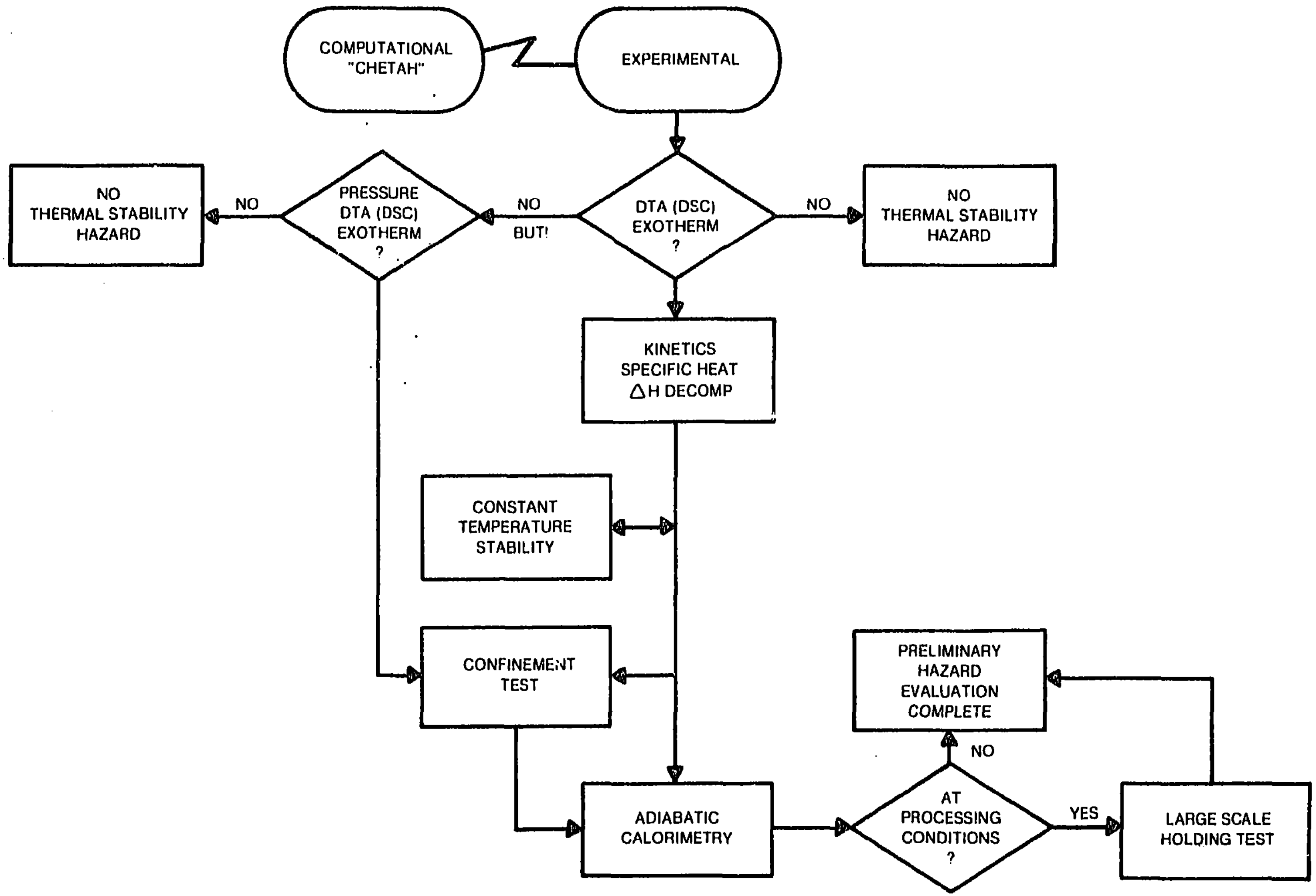

Fig. 1. Interrelationship of analytical procedures for thermal stability evaluation.

TABLE 2

CHETAH thermodynamic computations

Energy release appraisal	Tech safety			
Reactant compounds	AMT	MW	Ht formn.	Formula
S,*N*-Heterocycle	1.00	100	108.71	$C_xH_yN_zS$
Product compound(s)				
C	Carbon	*q* moles		
N2	Nitrogen	*z*/2		
S	Sulfur	1.00		
CH4	Methane	*r*		
Evaluation				

Criterion	Value	Rating
1	—1.04	High
2	—3.84	Medium
3	—135.2	Medium
4	100.8	Medium

The energy release potential of this mix is ... high ...

computations and/or experience. Under these circumstances, Seyler [7] has proposed the use of a pressure atmosphere in the differential thermal analysis.

The rate dependence of exothermic transitions must be minimized through isothermal heating to approximate the transition initiation temperature. Examination of Table 4 illustrates this time—temperature relationship. Such isothermal heating using differential thermal instrumentation has been referred to as "constant temperature stability" [8] testing and is generally

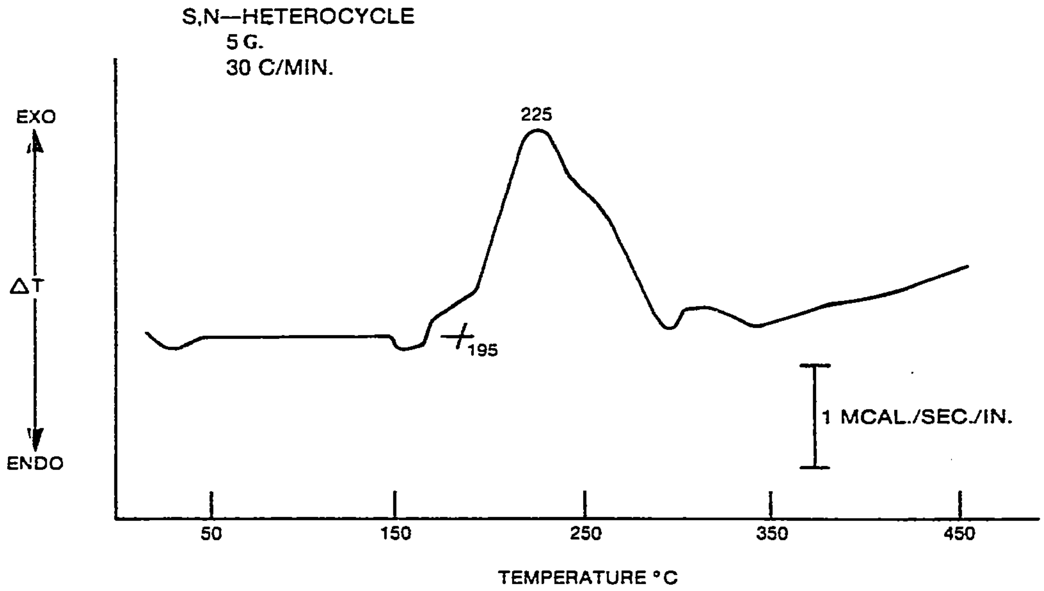

Fig. 2. Differential thermal curve of *S*,*N*-heterocyclic compound.

TABLE 3

Kinetic parameters using Ozawa's peak temperature method

Sample: *S,N*-heterocycle.

Heating rate (°C min^{-1})	Peak temp. (°C)	Log Z (min^{-1})	$1000/T$ (K^{-1})
2	205.8	10.2809	2.088
5	224.3	10.2276	2.010
10	235.9	10.2618	1.964
20	248.8	10.2796	1.916

Activation energy = 24.65 with std. dev. = 1.23 kcal mole^{-1}
Average pre-expon. factor = 1.83E + 10 min^{-1}
Average log Z = 10.2625
Slope = 5821.39 with std. dev. = 291.68
Intercept (y) = 12.44
RMSE = 3.017E—02

Extrapolated rates

Temp. (°C)	K (min^{-1})	Half-life (h)
25	1.568E—08	736618
40	1.140E—07	100421
55	7.033E—07	16425.5
100	6.711E—05	172.15
145	2.400E—03	4.8126
175	1.748E—02	0.66072
205	9.927E—02	0.11638

Isothermal aging confirmation: C/C_0 (theor.) = 61% for 298 min at 140°C.
C/C_0 (exptl.) = 58.8%.

used to measure the maximum temperature at which a material exists for 2 h without the evolution of heat.

A simultaneous release of volatile products accompanying an exothermic transition enhances the hazard potential; especially in a confined constant volume. Hence a "heating under confinement test" [9] is employed to measure the associated exothermic temperature rise, rate of pressure rise, and the maximum pressure generated by a material heated at 2—3°C min^{-1} while confined (Fig. 3). Relative simplicity of instrumentation and low cost suggest "heating under confinement" tests may be a substitute for differential thermal methods in screening for the presence of an exotherm. As a substitute technique for differential thermal methods, it is more time consuming, less sensitive, and not capable of providing quantitative thermal data.

Recent literature [10—13] has discussed the applicability of adiabatic calorimetry to thermal stability testing. Accelerating rate calorimetry (ARC) is a particularly suitable technique which involves step heating a material to a temperature at which it exhibits self-heating. At this temperature, the sys-

TABLE 4

Heating rate dependence of exothermic transitions

Condition	Temperature (°C)	Time (h)
Exotherm onset at 30°C min^{-1}	195	
Exotherm	190	0.4
Exotherm	135	16
Stable	100	17

tem is maintained adiabatically while both the time and pressure change are tabulated for unit increments of self-generated temperature rise. This data may be converted to an "adiabatic time to maximum rate" curve (Fig. 4), which can be adjusted for instrumental thermal inertia by the factor ϕ

$$\phi = 1 + \frac{C_{p(\text{bomb})} M_{(\text{bomb})}}{C_{p(\text{sample})} M_{(\text{sample})}} \tag{1}$$

where C_p is the specific heat and M the mass. Additional calculated data may be obtained from an ARC analysis including the reaction kinetics.

Although the combination of the above techniques give a reasonable prediction of thermal stability, an additional evaluation (thermal mass effects) may be necessary. The term "thermal mass effects" encompasses both synergistic and geometric influences on the thermal stability of larger masses of heated material. Consideration of the thermal mass effect is especially important when large quantities of solid material are to be handled at temperatures approaching the region of potential instability. Most testing for a ther-

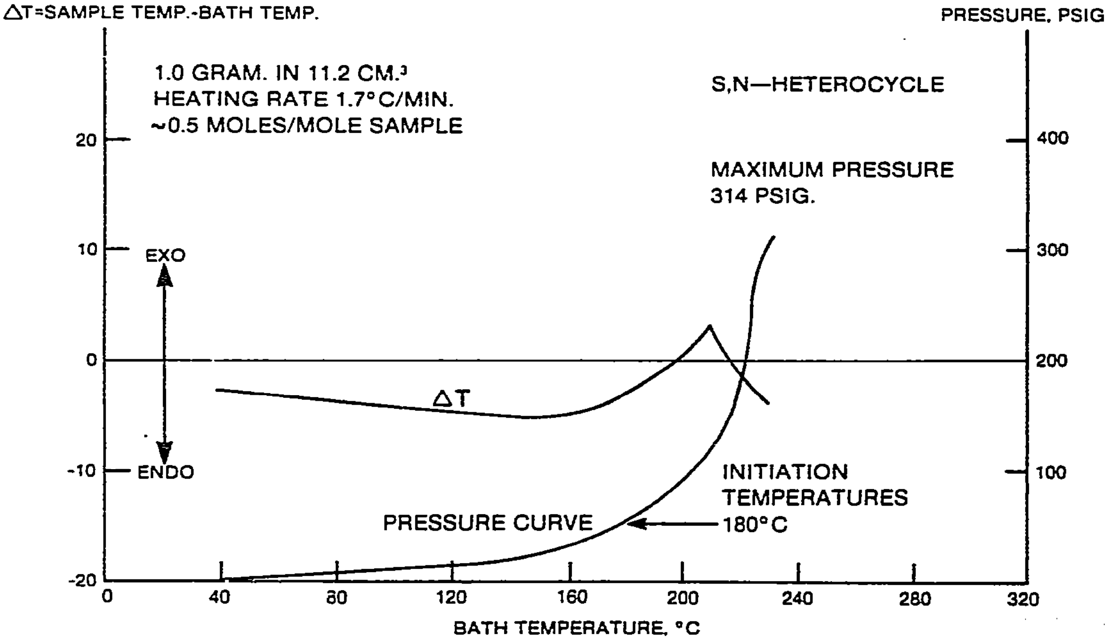

Fig. 3. Heating under confinement curves of *S,N*-heterocyclic compound.

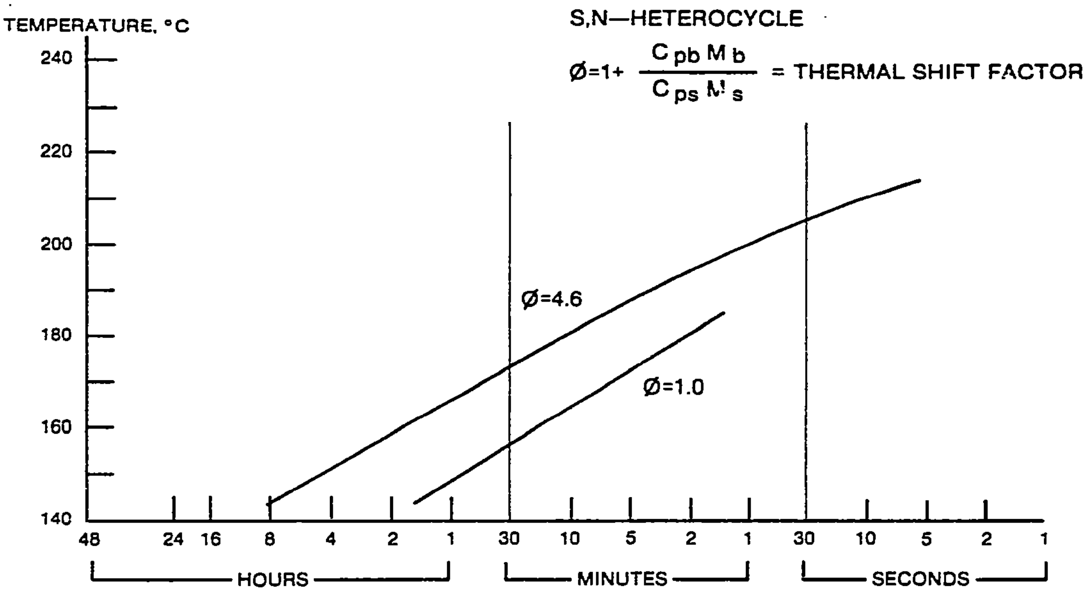

Fig. 4. Time to maximum rate curve of *S,N*-heterocyclic compound.

mal mass effect has, however, been characteristically non-uniform between laboratories. Typical sample sizes have ranged from several grams to many kilograms.

A particular thermal mass effect test used in the peroxide industry has been uniformly applied and is now being considered for general use by the ASTM E-27.02 committee. This self-accelerating decomposition temperature (SADT) test includes subjecting large samples contained in appropriate commercial packaging to a constant temperature oven until decomposition or a maximum of seven days has occurred.

CONCLUSIONS

A systematic application of thermal analytical tests for the assessment of the thermal stability of a *S,N*-heterocyclic sample compound has been demonstrated. This approach, using primarily ASTM recognized techniques, is suitable for general application.

It should be recognized that any thermal stability characterization is valid only for the sample and environmental factors employed. One only need glance at a "Chemical Safety" incident report to see numerous entries stating "this material was handled previously without any incident" to realize that this or any other program to assess the thermal stability of a material is at best representative and serves to minimize the associated potential hazards.

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