Thermochimica Acta, 39 (1980) 171—180

APPLICATION OF PRESSURE DTA (DSC) TO THERMAL HAZARD EVALUATION

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(Received 23 April 1979)

ABSTRACT

Any hazard evaluation program should necessarily include assessment of the thermal hazards of a material. To this end, differential thermal methods (DTA and DSC) are commonly employed. The utility of these methods in thermal hazard evaluation can be significantly extended if pressurized atmospheres are also employed. The characterization of volatile chemicals as much as 100°C beyond their atmospheric boiling temperature may be achieved with pressures under 1654 kPa (225 p.s.i.g.). The effective oxygen reactivity is enhanced with a pressurized air atmosphere. Also the confined conditions in a pressurized DTA (DSC) atmosphere produce results which can be used in many instances for the semi-quantitative assessment of the pressure—temperature change to be expected in more time-consuming "heating under confinements tests".

INTRODUCTION

An increasing awareness of and the need for public safety has been demonstrated through numerous governmental regulations concerning "chemicals" in industry. As a result, laboratories are asked to evaluate and classify chemicals as to their potential hazards. However, since no single test method could possibly establish the relative sensitivity of a chemical to all the various stimuli used in assessing a general hazard classification, what does one test for?

The approach to general hazard classification is typically to categorize hazard concerns such as toxicity, flammability, thermal stability, shock sensitivity etc. and evaluate them independently. Of specific concern in this paper is the assessment of thermal stability hazards of chemicals. The discussion to follow will concentrate on the extension of differential thermal techniques (DTA or DSC) in hazard classification through the use of a pressurized atmosphere.

INSTRUMENTATION

The differential thermal analyses were performed on a DuPont 990 thermal analyzer equipped with a Cell Base II module and a 2 mm capillary DTA furnace for ambient pressure. A compatible in-house fabricated pres-

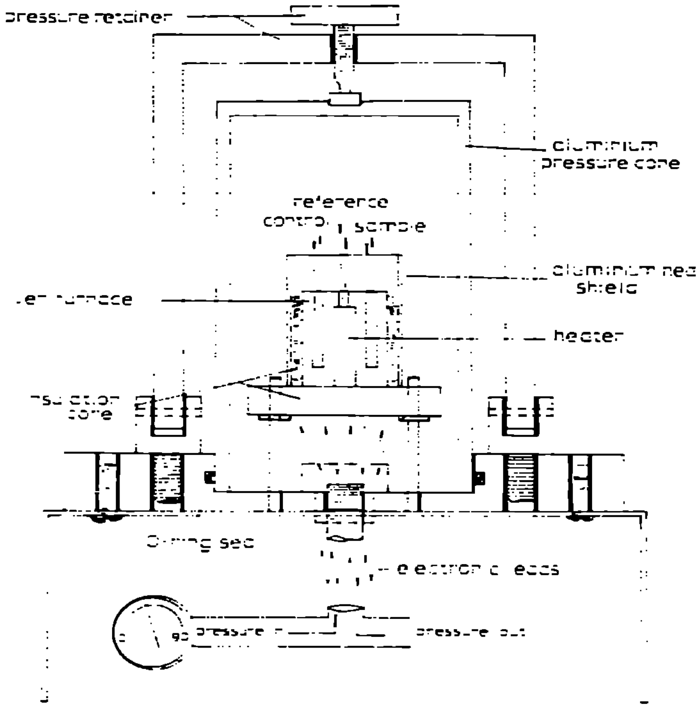

Fig. 1. Schematic of 4 mm capillary pressure DTA furance.

sure DTA cell was substituted for the pressure applications.

The pressure DTA cell as illustrated in Fig. 1 includes a 2.54 cm × 4.31 cm cylindrical silver furnace, a 9.5 mm diameter 100-W cartridge heater, a quartz insulation core, aluminum heat shield, an aluminum pressure cone, and a 2094 kPa (300 p.s.i.g.) pressure gauge. The furnace accommodates standard 4 mm capillary sample tubes into which chromel—alumel (Type K) thermocouples are inserted. Operation of the furnace has been accomplished at pressures to 1652 kPa (225 p.s.i.g.) of nitrogen, oxygen, or air.

DISCUSSION

Many compounds and mixtures, especially organic, contain sufficient energy such that under proper thermal conditions they could release a dangerously high concentration of energy [1]. A thermodynamic computational method, CHETAH [2], may be employed to predict the most energetic reaction (decomposition). However, the computational approach to thermal stability hazards cannot guarantee either safety or hazard and an experimental approach is necessary.

On can establish a general thermal stability classification for a chemical using the several techniques [3—5,7] listed in Table 1. A systematic application of these techniques such as outlined in Fig. 2 is recommended. The key to this approach is the observance of an exothermic transition during the "differential thermal" analysis. The lack of an exotherm constitutes no thermal stability hazard, while the presence of an exotherm necessitates

TABLE 1

Experimental techniques for thermal stability classification

Technique	Condition of interest
Differential thermal methods (DTA, DSC)	Presence of exotherm
Constant temperature stability (CTS)	Absence of exotherm for 2 h
Heating under confinement	Temperature and pressure change
Large-scale holding tests including adiabatic calorimetry	Thermal mass effect

additional testing to establish the temperature threshold and the magnitude of this heat release.

A serious shortcoming may be encountered with the analysis of a volatile chemical using differential thermal methods. Because vaporization is thermodynamically preferred over decomposition, all the sample is lost at its atmospheric boiling point. The result is no observed exotherm and consequently no thermal stability hazard; but is there? Volatile chemicals are generally handled in sealed containers, resulting in some equilibrium vapor phase which self-pressurizes the container. Under these conditions the chemical may be forced to remain in a condensed phase at temperatures above its normal boiling point.

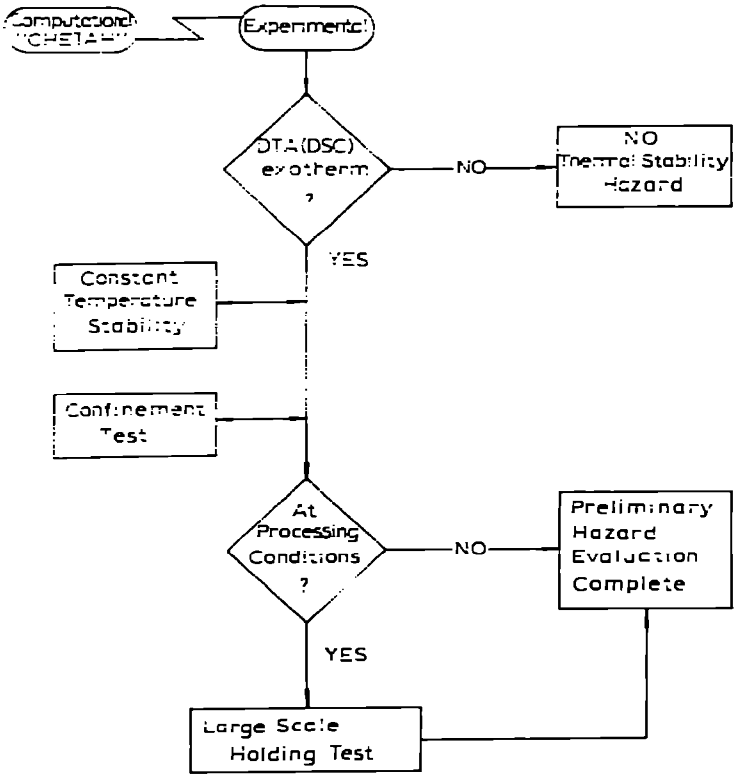

Fig. 2. Flow chart approach to a preliminary "thermal hazard evaluation."

Picture, if you will, a black drum of a highly volatile chemical inadvertently placed in direct sunlight on a hot summer day. After radiant heating has greatly elevated the internal temperature, the drum explodes. This situation definitely constitutes a hazard. Assuming the internal vapor pressure was not sufficient to cause drum rupture, it further constitutes a thermal stability hazard, a condition contrary to our hazard classification based on differential thermal methods recorded at atmospheric pressure.

Experience has shown that the application of a pressure of 1135 kPa (15) p.s.i.g.) will elevate the vaporization temperature as much as 100°C; therefore recording the DTA (DSC) of volatile chemicals at even moderate pressures serves to greatly extend the temperature range over which the thermal stability of the chemical may be assessed. As the example above suggests, many volatile organic chemicals will degrade rapidly if confined as a condensed phase at temperatures above their normal boiling point. Figure 3 illustrates this by comparing the DTA (DSC) curves for 2-chloro-3,5-dinitropyridine recorded at 101 kPa (15 p.s.i.a.) and 1240 kPa (165 p.s.i.g.). For this compound an initial exothermic reaction is observed within 20°C above the ambient boiling temperature. Because exothermic transitions are rate dependent, this difference between the boiling temperature and the decomposition temperature is actually less.

In addition to aiding the analysis of volatile chemicals beyond the normal vaporization temperature, a pressurized DTA (DSC) atmosphere also serves to enhance exothermic transitions. The fluoroborate material of Fig. 4 exhibits what appears to be a minor exotherm (T_{max} = 186° C) prior to endothermic decomposition with vaporization. In either air or nitrogen at 1135 kPa (150 p.s.i.g.) exothermic decomposition is clearly observed.

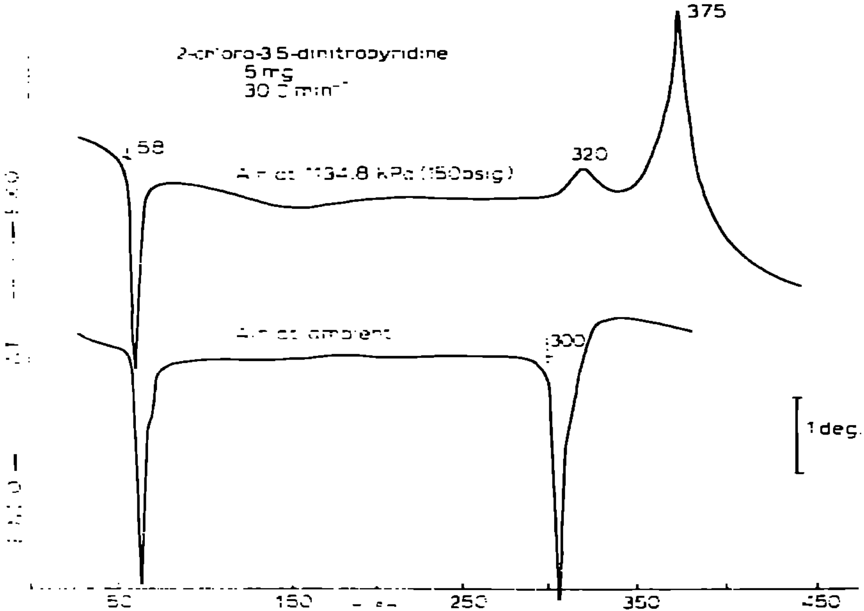

Fig. 3. DTA and pressure DTA curves for 2-chloro-3,5-dinitropyridine with experimental conditions as labeled.

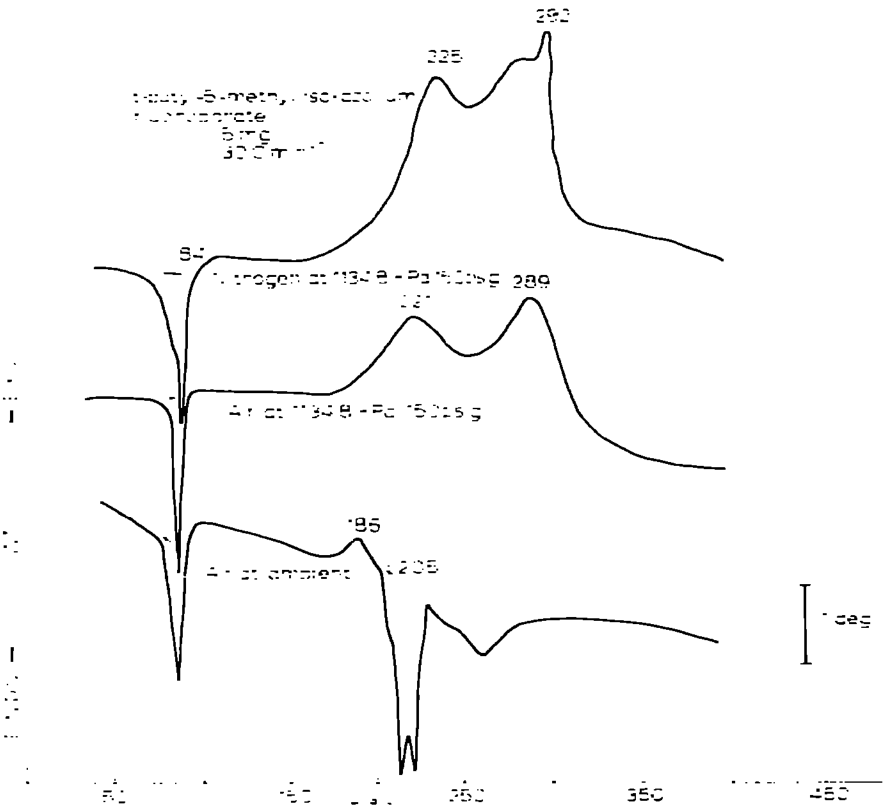

Fig. 4. DTA and pressure DTA curves for *t*-butyl-5-methylisoxazolium fluoroborate with experimental conditions as labeled.

Enhancement of decomposition exotherms is especially evident with reactive atmospheres such as air. An air atmosphere at 1135 kPa (150 p.s.i.g.) provides in effect, two atmospheres of pure oxygen to the sample—air interface. As a result, the pressurized atmosphere enhances the "reactivity" at the interface and thereby increases the rate of energy release for reactions involving oxygen. The occurrence of an exotherm ($T_{max} = 199°C$) for triallyl borate (Fig. 5) in only a pressurized air atmosphere exemplifies this enhanced oxygen reactivity.

Figure 6 offers additional evidence of the effectiveness of a pressurized DTA (DSC) atmosphere in establishing thermal hazards. This apparently thermally stable *t*-butylazidoformate exhibits extensive heat evolution in pressurized air. Such instability could pose a serious processing hazard, especially when considering the relatively low initiation temperature ($T_i \sim 110°C$).

A final application of pressure DTA (DSC) to thermal stability hazard classification is in its relationship to the "heating under confinement" test in Table 1. The confinement test [5] is designed to measure the temperature at which a material under confinement will react to generate heat and pressure while subjected to a slow (1—2°C min^{-1}) programmed temperature increase. The technique also provides a measure of the magnitude and rate

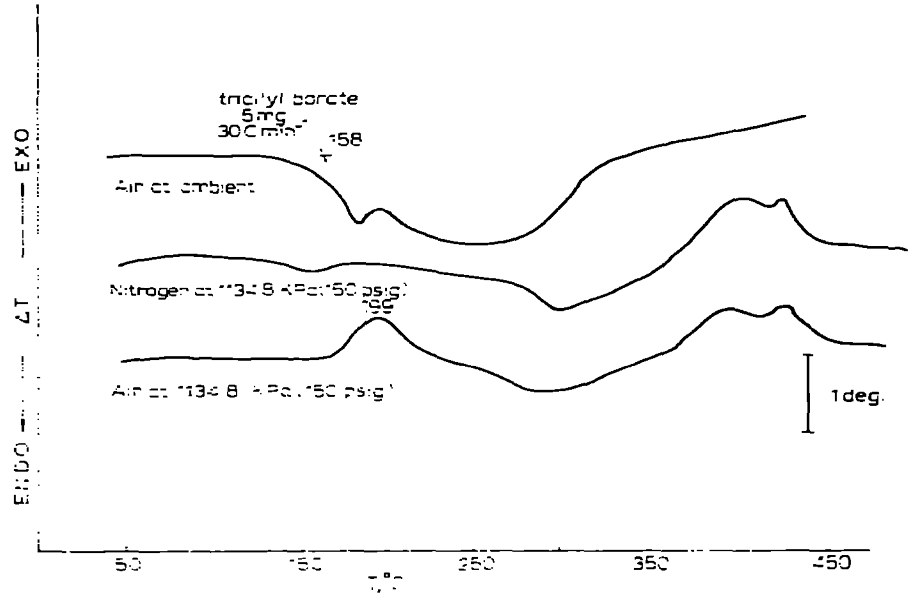

Fig. 5. DTA and pressure DTA curves for triallylborate with experimental conditions as labeled.

of pressure change associated with the exothermic reaction.

Confinement as used here refers to a condensed phase sample being sealed within a fixed volume under a given initial atmosphere. As such, the test configurations for both the "heating under confinement" test and the pressure DTA (DSC) are similar.

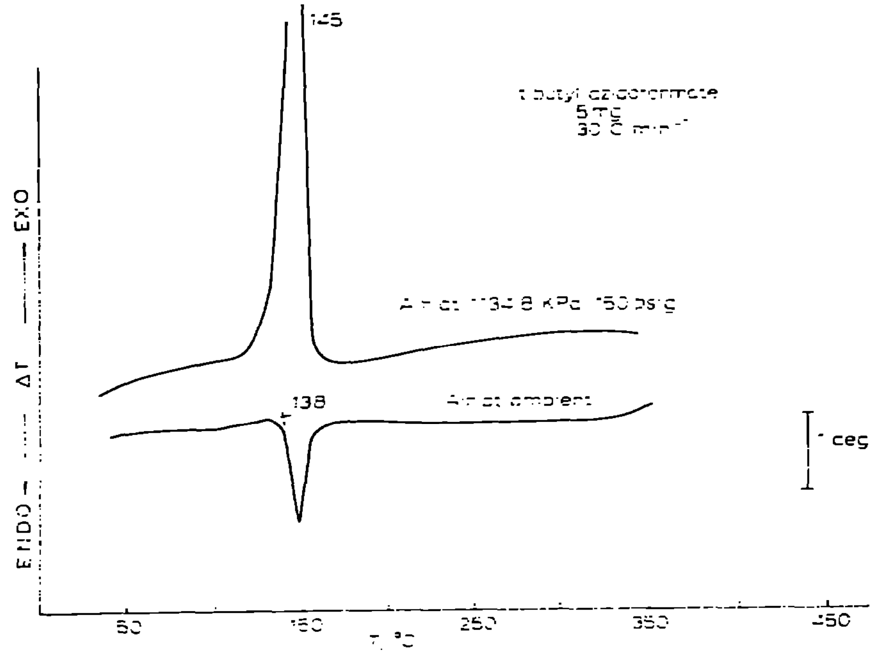

Fig. 6. DTA and pressure DTA curves for *t*-butylazidoformate with experimental conditions as labeled.

The rate dependence of exothermic transitions necessitates the use of very slow (<2.0°C min^{-1}) heating rates in the confinement test to best approximate the lowest initiation temperature. As a result of these slow rates the confinement test is time consuming and a means of screening samples for this test would be advantageous. The similarity of test configurations suggests the results of a pressure DTA (DSC) could be applicable as a means of screening chemicals for the slower confinement test. It should be noted, however, that the rate of heat generation observed by pressure DTA (DSC) does not necessarily provide a measure of any associated pressure change. Nevertheless, pressure DTA (DSC) has been successfully applied as a screening technique according to the scheme in Fig. 7. Use of the qualitative descriptors "weak moderate, strong, and severe" in Fig. 7 has been established from the pressure DTA instrumental response to a 5 mg sample heated at 30°C min^{-1} as described in Table 2 [6].

The observance of a moderate to severe exotherm by DTA (DSC) at atmospheric pressure establishes a thermal hazard. This therefore precludes the need for a pressure DTA (DSC) analysis, but requires a confinement test to evaluate the associated pressure change.

If "no exotherm" or a "weak exotherm" is observed by both atmospheric and pressure DTA (DSC), then confinement testing has generally been shown to be not necessary. But if the pressurized atmosphere results in an increase in the material's thermal instability, a confinement test would be recommended.

A comparison of results from "differential thermal" methods and the "heating under confinement" test may be made using Table 3. It can be observed from this comparison that the exotherm from pressure DTA (DSC) generally predicts the extent of pressure change associated with exothermic decomposition under "confinement". Not all exothermic transitions, however, involve decomposition and may thereby have little or no associated pressure rise. This could occur when the exothermic transition involves crystallization, chemical cross-linking, or other reactions producing nonvolatile products. This apparent failure in the pressure DTA (DSC) screening procedure is inconsequential in that the observance of an exotherm has already established a thermal hazard.

The above examples have demonstrated the need for and the effectiveness

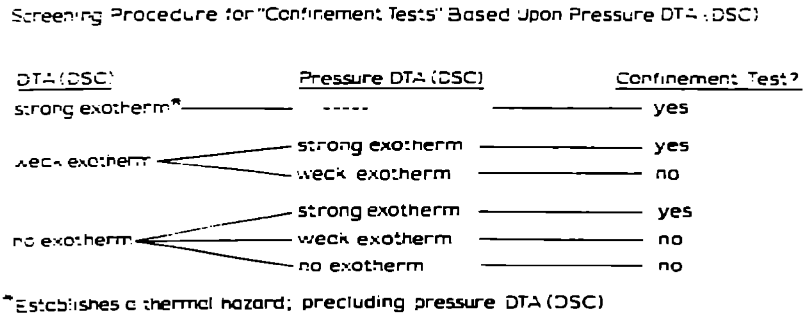

Fig. 7. Scheme for using pressure DTA data to evaluate the need for "confinement tests." The terms "strong" and "weak" are defined in Table 2.

TABLE 2

Classification of exotherm severity

Peak height (in.) [a]	Sensitivity (°C in^{-1})	Qualitative descriptor
<1	1	Weak
1—5	1	Moderate
1—2	5	Strong
<2	5	Severe

[a] Instrumental response based on 5 mg sample heated at 30°C min^{-1}.

of a pressurized DTA (DSC) analysis as part of any test program designed to assess a thermal hazard classification for chemicals. Incorporation of this method into such a test program may be visualized as the modification of the scheme of Fig. 1 to that given in Fig. 8.

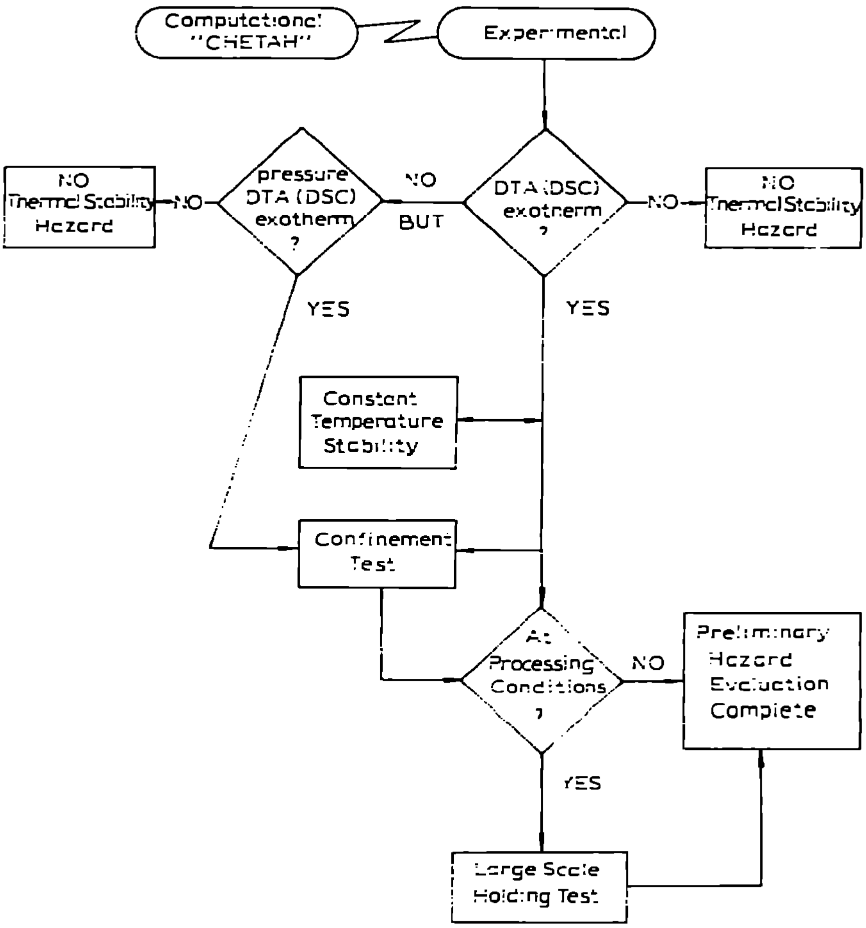

Fig. 8. Revised flow chart approach to a preliminary "thermal hazard evaluation".

TABLE 3

Comparison of DTA(DSC), pressure DTA(DSC), and confinement tests

Compound	DTA(DSC) exotherm		Confinement test		
	Ambient	Pressurized	Max. pressure (kPa)	Max. pressure rise (kPa sec^{-1})	Evolved gas (mole $mole^{-1}$)
5-Nitro-1H-indazole	None	Strong	8369	37895	1.6
Triallyl borate	None	Weak	680	6	0.2
t-Butyl-5-methyl-isoxazolium fluoroborate	Weak	Moderate	1080	29	0.4
t-Butylazidoformate	None	Severe	5338	24804	1.3
Aceto-2-(*p*-aminophenyl hydrazide)	Weak	Moderate	1514	0.35	0.3

CONCLUSION

The systematic use of a moderate 1135 kPa (150 p.s.i.g.) pressurized atmosphere in "differential thermal" analyses has been demonstrated to significantly improve one's ability to assess a thermal stability classification for chemicals. This improvement can be realized in three ways: (1) the condensed phase of volatile chemicals is retained for analyses as much as 100° C above the ambient pressure vaporization temperature; (2) the pressurized atmosphere may accentuate an otherwise questionable exothermic reaction. This is especially true when the reaction is oxygen limited. Under such circumstances, analysis in a reactive and an inert atmosphere may aid in distinguishing the mechanism: (3) pressure DTA (DSC) results may be applied to the screening of chemicals for more time-consuming "heating under confinement" tests.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the contributions of W.J. Fenlon and J.J. Wheeler of the Technical Safety Research Section of the Health, Safety and Human Factors Laboratory of Eastman Kodak Company.

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