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Using Screening Test Data to Classify Reactive Chemicals Hazards

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Abstract

The evaluation of reactive hazards is necessary for the safe working of the chemical process industries. An integral aspect of reactive hazard testing is the screening of chemicals to focus experimental efforts on the more hazardous chemicals. Screening is often performed using a Differential Scanning Calorimeter (DSC) or the Reactive System Screening Tool (RSST). The study of chemical compatibility highlights the need for efficient screening techniques, since a large number of experiments must be performed at a reasonable cost and in a short period of time. The purpose of this paper is to present chemical compatibility data measured using the RSST for di-ter-butyl peroxide (DTBP) in a variety of organic solvents. Analysis of the data with regard to the solvent functional groups was generalized to extend the measured data to compounds for which data are unavailable. Further, a classification for reactive chemicals is proposed that can serve as a guideline for selecting compositions for detailed testing.

Keywords: Reactive chemicals, RSST, onset temperature, heat of reaction, di-ter-butyl peroxide (DTBP), reactivity risk

Introduction

The assessment of reactive hazards is an important concern in the chemical process industry. Lack of accurate reactive chemistry knowledge of reactants, products, or intermediates has been a cause of numerous incidents [1,2]. Often, subtle changes during plant operations may lead to temperatures and pressures that can initiate runaway reactions [3]. Sometimes the reactivity information can be obtained from literature sources, but if essential information is not available, reactive hazards are generally estimated using calorimetric techniques. A small amount of the sample is heated over a range of temperature (usually within 30 °C – 400 °C), and temperature, pressure and time data are recorded. This information is then used for alarm settings, relief sizing, and modeling. Before a detailed testing is performed, screening tests are performed [4] using calorimeters such as a

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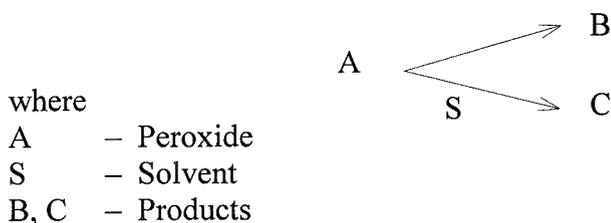
Differential Scanning Calorimeter (DSC) or the Reactive System Screening Tool (RSST) [5]. Such screening tests are relatively inexpensive and can be performed quickly.

The issue of chemical compatibility places an additional emphasis on efficient screening procedures since numerous systems have to be tested. A detailed testing using the Vent Size Package (VSP) [5] or the Automated Pressure Adiabatic Calorimeter (APTAC) [6] may not be possible on all likely combinations of chemicals. Efficient screening techniques should be developed to obtain the requisite data in a short period of time to utilize minimum resources. The knowledge of chemistry can be applied to extend the measured data to systems where data are unavailable. It is important that this knowledge be available during the process design stage to develop a safer and more efficient process. The Mary Kay O'Connor Process Safety Center (MKOPSC) is gathering reactivity data on a variety of systems and will make them available to industry personnel.

The purpose of this paper is to employ the RSST to estimate reactive hazards due to compatibility of di-ter-butyl peroxide (DTBP) with a variety of organic solvents. The data can be extended to other organic solvents with similar functional groups and can be helpful in selecting process conditions. Furthermore, a classification for reactive chemicals is proposed that would help to identify the more hazardous compositions. Such a classification is designed to select chemicals for detailed testing and it can be refined to develop a generalized classification for reactive chemicals.

Details of the test system

Peroxide and hydroperoxide compounds are commonly used as radical initiators in the chemical and petrochemical industries and are known to be thermally unstable [7]. These compounds are susceptible to violent decomposition that can be initiated by heat, mechanical shock, or friction, especially in presence of certain catalysts [8]. The highly reactive behavior of peroxide and hydroperoxides is attributed to the weak O-O linkage in these compounds. Pure organic peroxides are extremely reactive and therefore are often diluted with organic solvents to reduce or control reactivity. Solvent may modify the decomposition pathway of the peroxide, however, and the new routes may be sources of potential reactive hazards. For example, diethyl ether can form an explosive mixture with organic peroxides [8]. The following steps are involved in the decomposition of peroxides in the presence of a solvent:



The peroxide can decompose to B or C depending on the interaction with the solvent, S. The problem is exemplified with di-ter-butyl peroxide (DTBP) as the sample system. It has been reported that DTBP undergoes an unimolecular first-order decomposition in the gas phase and in the presence of solvents such as benzene, toluene, cyclohexane, cumene, tri-n-butylamine, and t-butylbenzene [9]. However, in the presence of primary and secondary alcohols, the overall reaction is still first order in peroxide but the rate of reaction is faster [10]. Although there is a considerable body of literature describing the thermal decomposition of organic peroxides in various organic solvents, it is not clear on a mechanistic level how the solvent influences the decomposition pathway or under what conditions the resulting reactions may pose potential hazards.

Experimental details

There are various calorimeters available for performing reactive hazard assessments. Generally, the chemicals are screened using a DSC or the RSST and more detailed testing can be performed using other calorimeters such as the APTAC or the VSP. A comparison of three available calorimeters is presented in Table 1.

Calorimeter	Capital Cost	Time reqd. for a run	Sample size	Scanning Rate ($^{\circ}\text{C}/\text{min}$)	Data obtained	Comments
DSC	1 \$	1 hr	1-10 mg	10	T vs. time	Popular method to screen reactive hazards
RSST	1.5/2 \$	6 hrs	Up to 10 ml	1-5	T,P vs. time	Open cell; data can be used for relief sizing
APTAC	20 \$	12-16 hrs	Up to 130 ml	1-2	T,P vs. time	Maintains adiabatic conditions; maintenance intensive

Table 1. Comparison of available calorimeters

For this project, the calorimetric experiments were performed using the RSST from Fauske & Associates. The RSST uses a 10-ml contained in an open, well-insulated glass test cell and allows scanning rates up to $2^{\circ}\text{C}/\text{min}$. A cross-section of the RSST is shown in Figure 1. The RSST is used for screening reactive hazards, since it provides temperature, pressure vs. time data at a moderate cost compared to the APTAC or VSP.

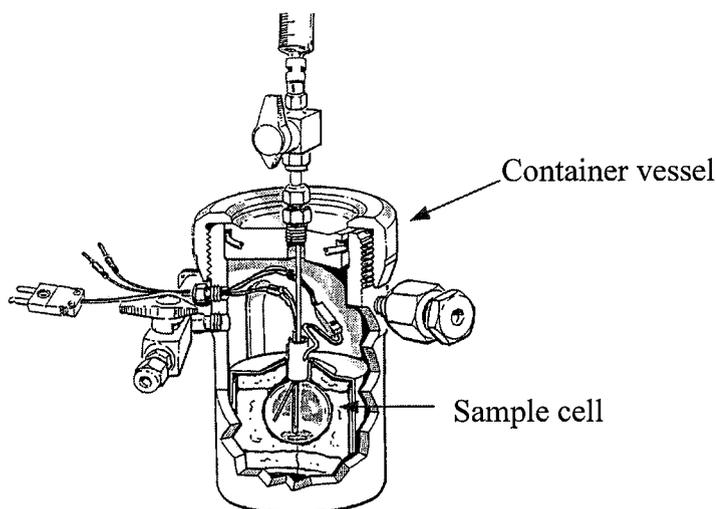


Figure 1. RSST (by permission, Fauske & Assoc.)

Nine solutions were each prepared by combining 10 gm of a 30 wt % DTBP with each of the following nine solvents: methanol, chlorobenzene, n-butylamine, t-butanol, n-butanol, cyclohexane,

toluene, tetrahydrofuran (THF), and acetone. A minimum of two runs were performed for each composition with a back-up pressure of 350 psi and a heating rate of 1 °C/min. A sample plot of temperature vs. time for 30 wt % DTBP in the nine organic solvents is shown in Figure 2.

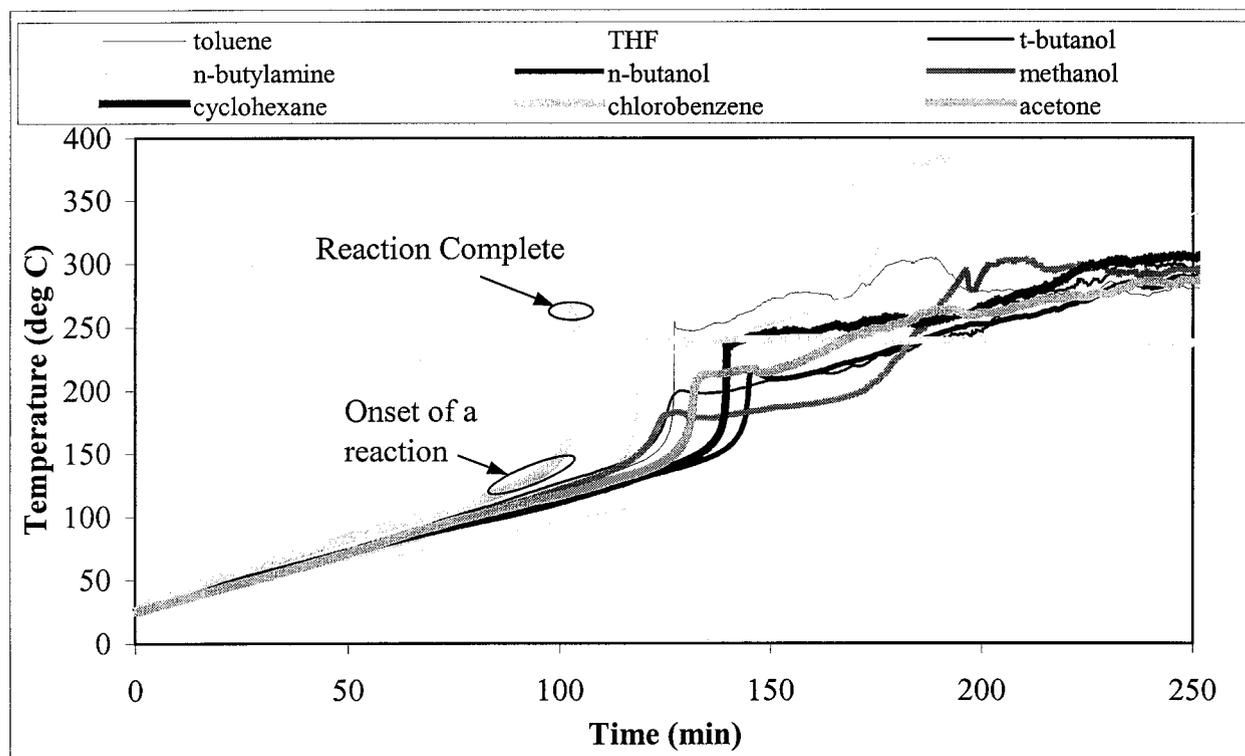


Figure 2. Decomposition behavior for 30 wt % DTBP in organic solvents

Discussion of results

The screening tests yields a preliminary indication of temperature beyond which exothermic activity is observed and the magnitude of the exotherm. Such data can help assess the potential reactive hazards posed by a chemical or composition.

The temperature at which a system first exhibits exothermic activity is called the onset temperature (T_o) and denotes a rate of a chemical reaction significant enough to be measured by the calorimeter. The detected onset temperature is thus a measure of the reaction kinetics. Although there is considerable argument over its interpretation [11], for selecting appropriate process temperatures, the onset temperature is an important parameter at the screening level of testing. In this regard, Ando et al. have proposed that onset temperature be used as a parameter to classify reactive chemicals [12].

The energy released ($-\Delta H$) during the process is calculated using the following formula:

$$-\Delta H = \Phi m C_p (T_{\max} - T_o)$$

where

$$\Phi = \frac{m_s C_{ps} + m C_p}{m C_p} - \text{Phi factor}$$

m_s – Mass of the sample cell

C_{ps} – Heat capacity of the sample cell

m – Mass of the sample

C_p – Heat capacity of the sample

T_{\max} – Maximum temperature attained by the sample during the reaction

From the calorimetric data, the rate constant for the reaction is obtained using the following formula:

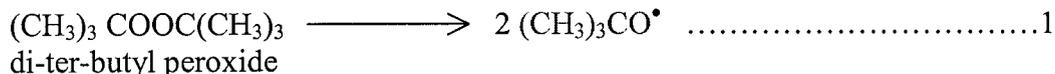
$$k = \frac{\frac{dT}{dt}}{\left(\frac{T_{\max} - T}{T_{\max} - T_o}\right)^n (T_{\max} - T_o)}$$

where

n – order of the reaction

Thus, the overall thermodynamics and kinetics of a reaction can be estimated from temperature-time calorimetric data. Therefore, the onset temperature (T_o) and heat of reaction ($-\Delta H$), two important parameters at the screening level of testing, can be easily determined from the temperature-time data.

The onset temperatures and heats of reaction for 30 wt % DTBP in the nine organic solvents are summarized in Table 2. Included are the maximum rates of increase of temperature and pressure and the bond strengths of the -O-O- bond in the solvents. The bond strength calculation is based on the energies of the species involved in the following reaction, which is believed to be the rate-limiting step in the DTBP decomposition:



The bond strength calculations were performed using the Gaussian 98 suite of programs [13] with the density function model B3P86 [14] and the cc-pVDZ basis set [15]. The optimized geometries were obtained for the species, and single point energies were then computed using the polarized continuum model (PCM) [16] to account for the effect of the solvent on the -O-O- bond dissociation energy (BDE).

Sr. no.	Solvent	Tonset °C	Tmax °C	(dT/dt)max °C/min	(dP/dt)max psi/min	Heat of reaction kcal/mol	BDE kcal/mol
1	methanol	117	180	10	7	16.7	33.7
2	chlorobenzene	120	260	1000	1000	24.3	33.8
3	n-butylamine	125	230	220	400	26.4	33.8
4	t-butanol	130	200	15	18	18.0	33.8
5	n-butanol	130	210	43	33	23.8	33.8
6	cyclohexane	133	240	300	633	22.9	37.2
7	toluene	135	250	700	900	23.3	37.4
8	tetrahydrofuran	135	243	425	1000	21.9	36.3
9	acetone	138	205	35	65	16.1	36.1

Table 2. Summary of data for 30 wt % DTBP in various solvents

The calculations show that the decomposition of DTBP is initiated within 115-135 °C depending on the solvent, and the -O-O- bond strengths in the nine solvents are within 33-37 kcal/mol. The heat of reaction for DTBP decomposition are within 15-25 kcal/mol depending on the solvent. The overall extent of reactive hazards for DTBP in these nine solvents appears to be comparable.

The reactive hazards can be further generalized to similar types of chemicals. For example 30 wt % DTBP has comparable behavior in toluene and cyclohexane, and it is expected to exhibit a similar behavior in other organic liquids such as benzene. Likewise the reactive behavior of DTBP in ketones is expected to be similar to the behavior in acetone. Thus knowledge of functional groups can be used to extend data obtained on DTBP to estimate compatibilities of DTBP with other chemicals.

Proposed classification

It is important to perform detailed analyses on the more reactive systems. However there is no common consensus among researchers on the attributes of a system that qualify it for a more sophisticated testing. We therefore propose a classification based on the onset temperature (Tonset) and the heat of reaction (-ΔH) of a compound as shown in Figure 3. As indicated, the chemicals can be divided into the following four classes:

1. Class I: These compounds react at low temperatures liberating a large amount of heat.
2. Class II: The compounds react with significant heat release at higher temperatures.
3. Class III: The compounds react at low temperatures, similar to compounds in Class I, but the reaction is not so exothermic as for the chemicals in Class I.
4. Class IV: These chemicals react at higher temperatures and are mildly exothermic.

Thus, the reactive hazard decreases from Class I to IV. The more hazardous chemicals are in Class I, since they decompose at lower temperatures and release a large amount of heat. These are also the

chemicals that are more likely to decompose violently and should be carefully handled and thoroughly tested. The chemicals in Class II also lie in the high hazard category since they release a large amount of energy, and chemicals in Classes III and IV pose medium and low risk, respectively.

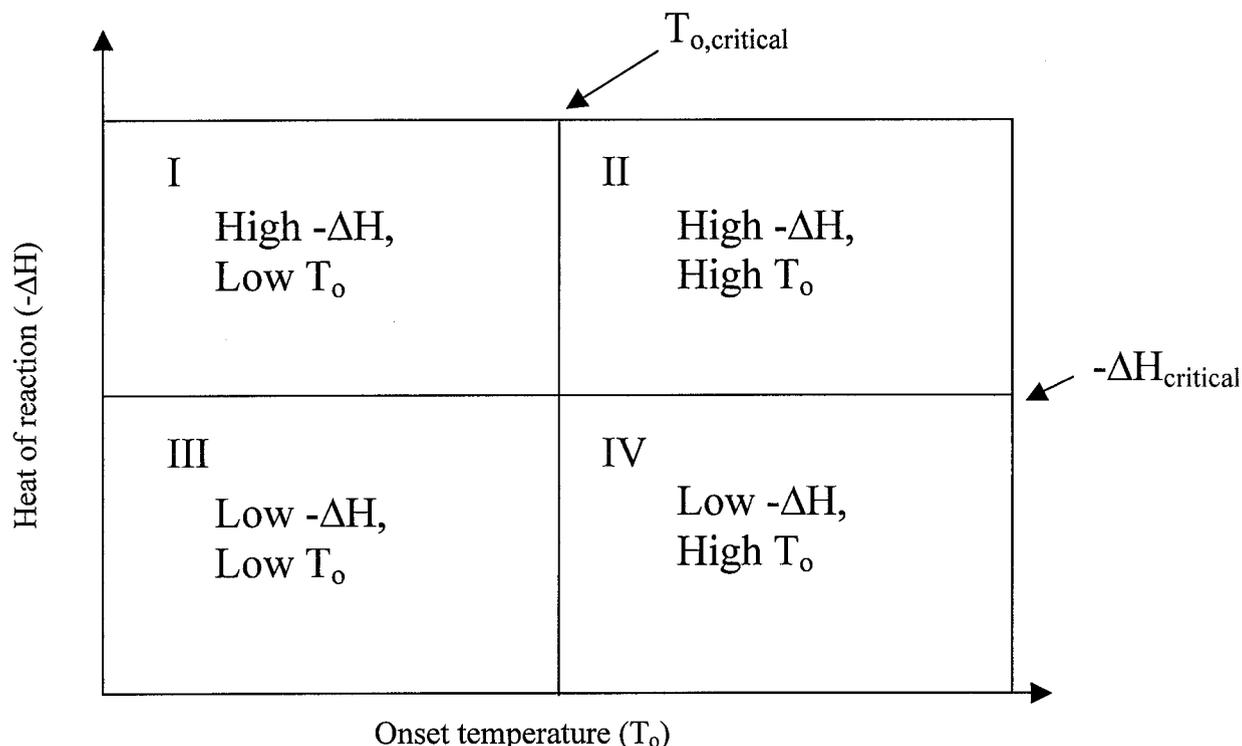


Figure 3. Proposed classification for reactive chemicals

Choice of critical values

The classification places rigid boundaries based on the values for onset temperature and heat of reaction for a chemical or composition. These rigid boundaries can be avoided by the use of fuzzy logic to define the bounds, however our aim is to demonstrate a basis for reactive chemical classification. With the static limits the choice of threshold values is subject to judgment, and choices of these values are discussed below.

We recommend a value of 200 °C for the critical onset temperature $T_{0,critical}$. This value is in agreement with the NFPA intrinsic thermal stability rating [17], which classifies materials that exhibit adiabatic exothermic initiation temperatures below 200 °C as more hazardous and specifies a hazard rank of 2.

Trinitrotoluene (TNT) is considered to be a highly energetic material and is used as an explosive. The amount of energy released due to decomposition of TNT is ~ 290 kcal/mol [12]. The critical value for the heat of reaction can be set to about half of the energy released due to TNT decomposition, or ~ -150 kcal/mol. The ASTM CHETAH program [18] calculates the maximum heat of decomposition based on the heat of formation, and if the maximum heat of decomposition is more exothermic than -2.929 kJ/g it classifies the material as hazardous. Thus -3 kJ/g (-0.7 kcal/g) can be selected as a critical threshold value for the heat of reaction, $\Delta H_{\text{critical}}$, for which we recommend a value of -150 kcal/gmol.

A plot of T_{onset} vs. heat of reaction for DTBP in the nine solvents is shown in Figure 4, which shows that all the compositions lie in Class III, as illustrated in Figure 3. These results suggest that significant decomposition of 30 wt % DTBP in organic solvent can be initiated at temperatures lower than 200 °C, but the heat released during the reaction is much less than the heat released during TNT decomposition. Based on the tests carried out at the screening level, detailed testing of these mixtures may not be necessary unless the operating temperature is greater than ~ 100 °C.

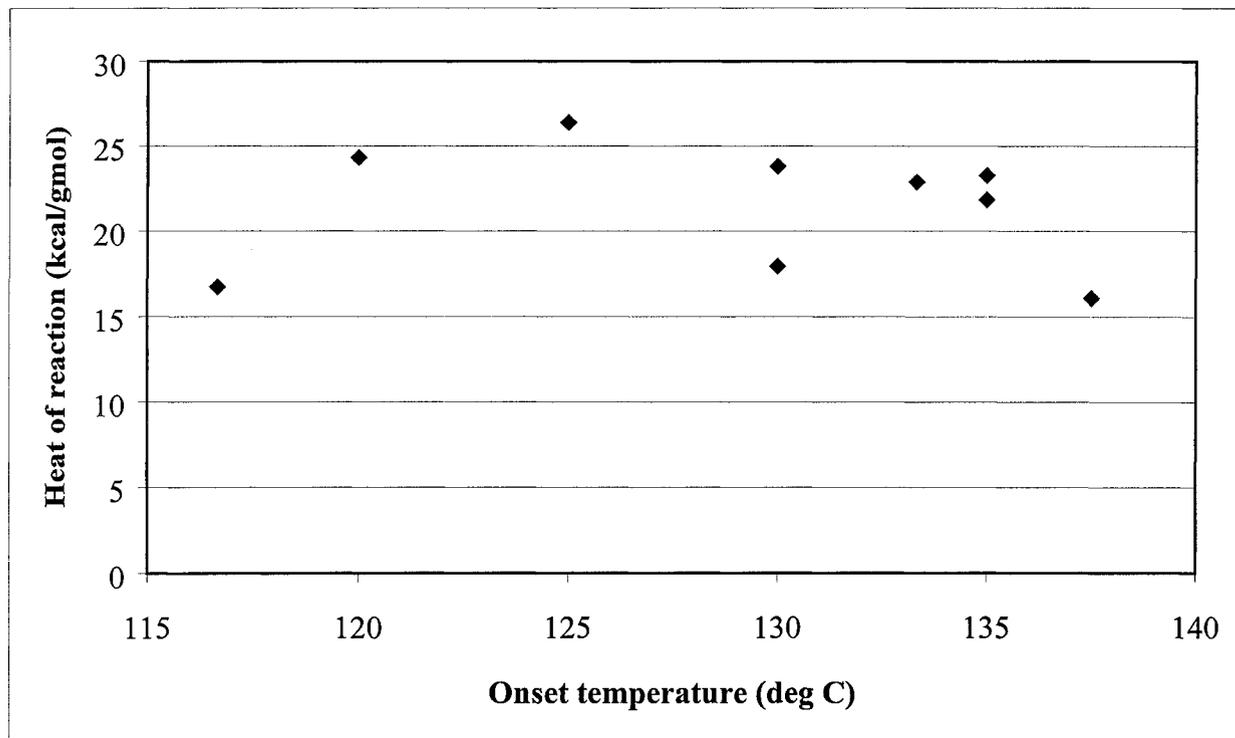


Figure 4. Heat of reaction for DTBP in the nine solvents

It is worth noting that increasing the concentration of DTBP in these solvents should result in lower onset temperatures and larger amounts of released heat. Higher concentration DTBP solutions may therefore reside in Class I, and detailed testing may be required.

Calorimetric data for selected compounds [12] are listed in Table 3 and are assigned to the four reactive classes based on the values for $-\Delta H$ and T_o and displayed in Figure 5.

Sr. no.	Compound	Onset temperature (°C)	Heat of reaction (kcal/gmol)
1	p-Nitrotoluene	366	51
2	3,5 Dinitrobenzoic acid	374	161
3	Trinitrotoluene	314	292
4	Benzoyl peroxide	108	107
5	t-butyl hydroperoxide	98	23
6	Cumene hydroperoxide	187	68
7	Xanthene	190	15
8	Benzyl chloride	172	34
9	2-Bromo-n-butyric acid	91	52

Table 3. DSC data for various compounds [12]

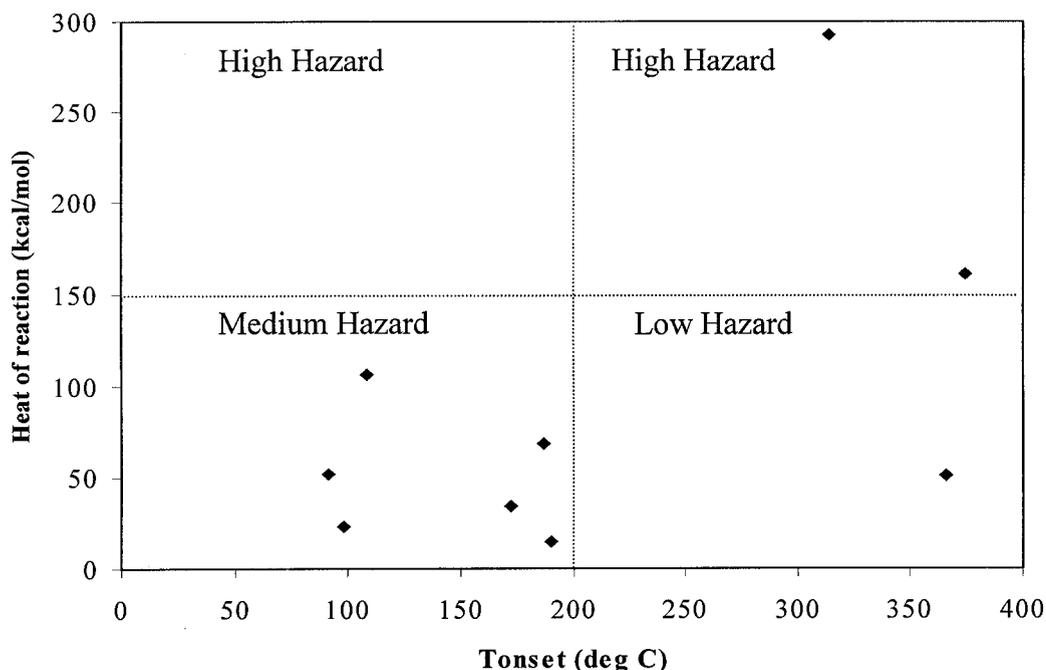


Figure 5. Calorimetric data on selected compounds [12]

We consider that the classification proposed above is simple yet effective and can be refined for classification of reactive chemicals and developing hazard rankings for various compositions and conditions. A comprehensive and realistic risk assessment would involve also the process temperature for a particular system. We therefore propose a normalized classification based on the

heat of reaction and the onset temperatures. The onset temperature is the detected onset temperature and depends on the sensitivity of the calorimeter and the run conditions. However, the closer the system is to this detected onset temperature, the higher the probability it will undergo significant reaction. We can thus define a temperature safety ratio (τ) as:

$$\tau = T_{\text{process}} / T_{\text{onset}}$$

where the smaller the value of τ , the safer the process. With its relationship to the available thermal energy (related to T_{process}) and the energy required for thermal activation (related to T_{onset}), τ is a measure of the reaction kinetics. With increasing temperature, the rate of reaction increases in an exponential fashion according to the Arrhenius equation:

$$k = A \exp(-E_a/RT)$$

where

k – rate constant

A – frequency factor

E_a – activation energy

R – gas constant (1.987 cal/gmol K)

The amount of energy released by the reaction depends on the heat of reaction ($-\Delta H$). We can thus define another ratio, β , as the amount of energy released to the energy released by TNT.

$$\beta = -\Delta H / 290$$

β is thus a thermodynamic quantity and is a measure of the energy release potential of a substance. Also, τ is a measure of probability of reaction occurrence, and β is a measure of the consequence of the reaction. The product of the two ratios τ and β is therefore a measure of risk involved due to thermal instability in processing or storing a chemical at a particular temperature. We can express this risk quantitatively by defining a reactivity risk index (RRI), as follows:

$$\text{RRI} = \tau * \beta = \{T_{\text{process}} / T_{\text{onset}}\} \{-\Delta H / 290\}$$

The lower the value of the product, $\tau * \beta$, the lower the risk due to lower thermal instability and/or lower energy released from thermal decomposition of a substance.

Conclusions

The RSST was employed to evaluate thermal instability hazards of 30 wt % DTBP in a variety of organic solvents in which the reactive nature of the DTBP appears to be comparable. The systems studied were a part of a larger effort at the MKOPSC to generate reactivity data for potentially reactive chemicals and compositions. A classification is recommended for the reactive chemicals to identify the more hazardous compositions. This classification takes into account the onset temperatures and the amount of energy released during the reaction and could be refined and adopted as a useful tool for reactive chemical hazard assessment. Also, a reactivity risk index, RRI, is defined for a chemical substance as a guide for reactivity risk evaluation.

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