



Using screening test data to recognize reactive chemical hazards

Sanjeev R. Saraf, William J. Rogers, M. Sam Mannan*

Department of Chemical Engineering, Mary Kay O'Connor Process Safety Center, Texas A&M University, College Station, TX 77843-3122, USA

Abstract

The evaluation of reactive hazards is necessary for safe operations in 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 incompatibility 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. A purpose of this paper is to present chemical incompatibility data measured using the RSST for di-tert-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.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Reactive chemicals; RSST; Onset temperature; Heat of reaction; Di-tert-butyl peroxide (DTBP); Reactivity risk index

1. 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

* Corresponding author. Tel.: +1-979-862-3985; fax: +1-979-458-1493.
E-mail address: mannan@tamu.edu (M.S. Mannan).

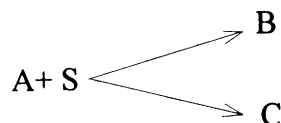
within 30–400 °C), and temperature, pressure, and time data are recorded. This information is then used for alarm settings, relief sizing, and hazard assessments. Prior to detailed testing, screening tests are performed [4] using calorimeters such as a Differential Scanning Calorimeter (DSC) or the Reactive System Screening Tool (RSST) [5]. Such screening tests are relatively inexpensive and can be performed quickly.

The issue of chemical incompatibility places an additional emphasis on efficient screening procedures since numerous systems must be tested. 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 measured data to systems where data are unavailable. It is important that this incompatibility knowledge be used during the process design stages for development of safer and more efficient processes. 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.

A purpose of this paper is to employ the RSST to estimate reactive hazards due to behavior of di-tert-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.

2. 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. However, the solvent can affect the reaction rate and also may modify the decomposition pathway of the peroxide, and the new routes may be sources of additional reactive hazards. For example, diethyl ether can form an explosive mixture with organic peroxides [8]. The following paths represent decomposition of peroxides in the presence of a solvent:



where A is the peroxide; S is the solvent; B, C are the products.

The peroxide can decompose to B or C depending on the interaction with the solvent, S. The solvent can affect the decomposition rate of A along the first path to B or react

with A along the second path to C. The problem is exemplified with DTBP as the sample system. It has been reported that DTBP undergoes 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 that pathway may pose potential hazards.

3. 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.

For this study, the calorimetric experiments were performed using the RSST from Fauske and Associates. The RSST accommodates a 10-ml sample in an open, well-insulated glass test cell and provides scanning rates up to 2 °C/min and temperature, pressure versus time data at a moderate cost compared to the APTAC or VSP. A cross-section of the RSST is shown in Fig. 1.

Nine solutions of 30 wt.% DTBP were prepared 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 RSST runs were performed for each composition with an imposed back-up nitrogen pressure of 350 psia and a heating

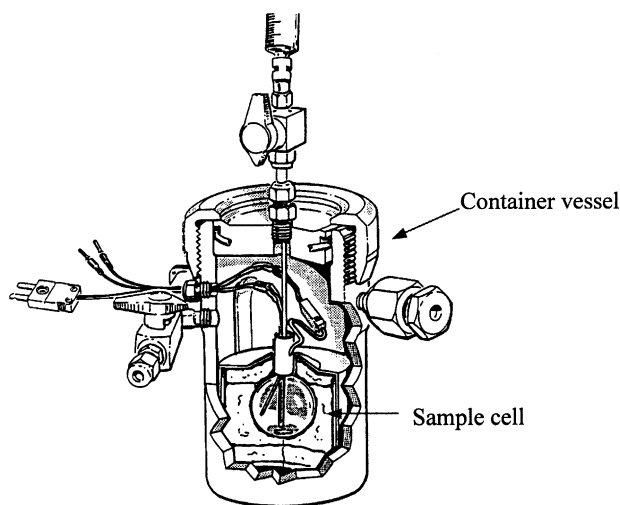


Fig. 1. RSST (by permission, Fauske and Associates).

Table 1
Comparison of available calorimeters

Calorimeter	Capital cost ^a (\$)	Time required for a run (h)	Sample size	Scanning rate (°C/min)	Data obtained	Comments
DSC	1	1	1–10 mg	10	<i>T</i> vs. time	Popular method to screen reactive hazards
RSST	1.5/2	6	Up to 10 ml	1–5	<i>T, P</i> vs. time	Open cell; data can be used for relief sizing
APTAC	10	12–16	Up to 130 ml	1–2 ^b	<i>T, P</i> vs. time	Maintains adiabatic conditions; maintenance intensive

^a Relative.

^b Not a fixed scanning rate.

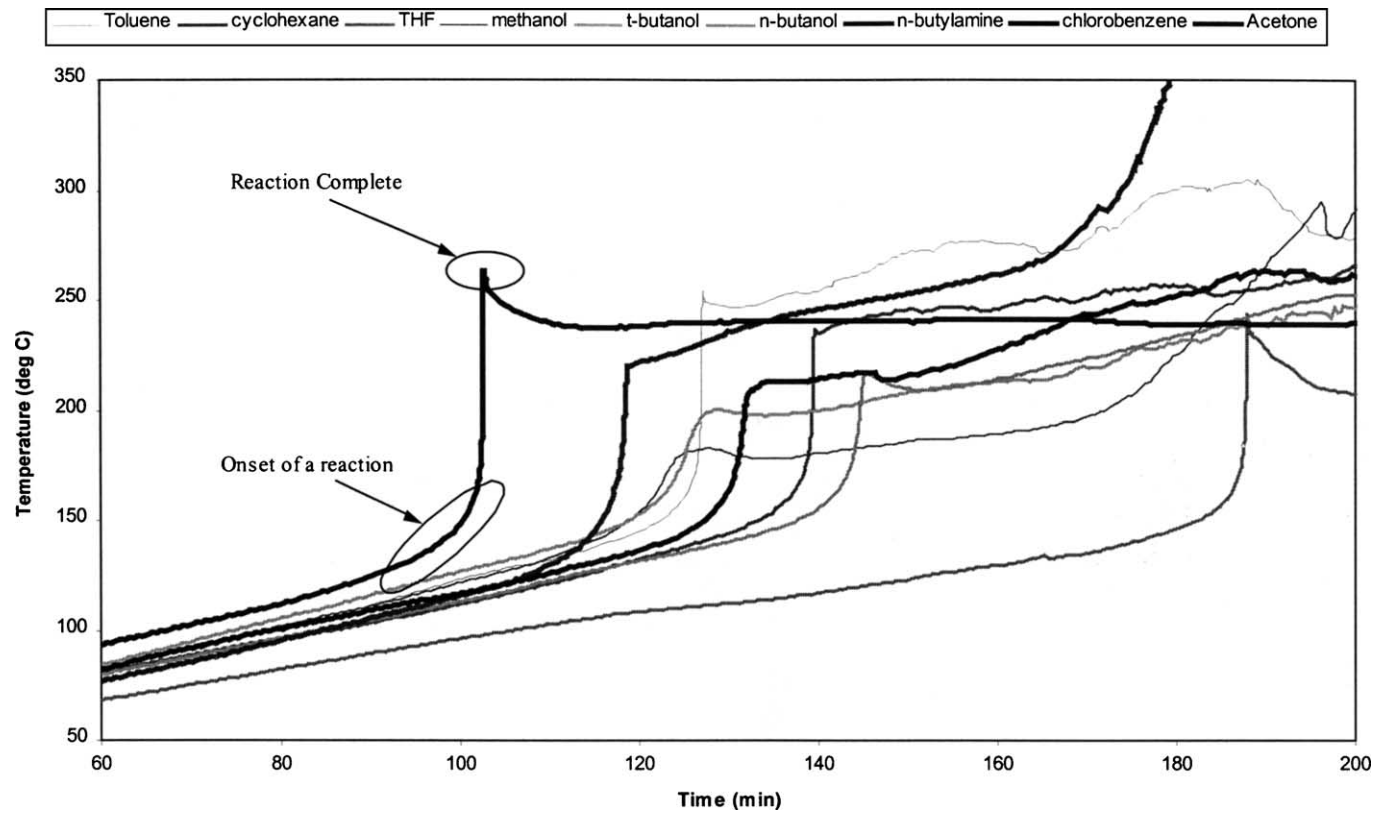


Fig. 2. Decomposition behavior for 30 wt.% DTBP in various organic solvents.

rate of 1 °C/min. A sample plot of temperature versus time for 30 wt.% DTBP in the nine organic solvents is shown in Fig. 2.

4. Discussion of results

The screening tests yield 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_{onset}) and denotes a sufficiently rapid rate of a chemical reaction to be measured by the calorimeter. The detected onset temperature is thus a measure of the reaction rate. 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 a process is calculated using the following formula:

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

where

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

m_s is the mass of the sample cell, C_{ps} is the heat capacity of the sample cell, m is the mass of the sample, C_p is the heat capacity of the sample (average over T_{onset} , T_{max}), T_{max} is the maximum temperature attained by the sample during the reaction.

From the calorimetric data, the rate constant, k , for a single n th order power-law reaction is obtained using the following formula [13]:

$$k = \frac{dT/dt}{((T_{\text{max}} - T)/(T_{\text{max}} - T_{\text{onset}}))^n (T_{\text{max}} - T_{\text{onset}})}$$

where n is the order of the reaction.

Thus, the overall thermodynamics and kinetics of a reaction can be estimated from temperature–time calorimetric data. Also, the onset temperature (T_{onset}) 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 RSST onset temperatures, for which the self-heat rate was ~ 0.3 °C/min, 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:

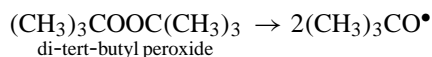


Table 2
Summary of RSST data for 30 wt.% DTBP in various solvents

Serial number	Solvent	T_{onset} (°C)	T_{max} (°C)	$(dT/dr)_{\text{max}}$ (°C/min)	$(dP/dr)_{\text{max}}$ (psi/min)	Heat of reaction (cal/g)	BDE (kcal/mol)	RRI (75 °C)
1	Methanol	117	180	10	7	126	33.7	0.32
2	Chlorobenzene	120	260	1000	1000	117	33.8	0.30
3	<i>n</i> -Butylamine	125	230	220	400	167	33.8	0.42
4	<i>t</i> -Butanol	130	200	15	18	163	33.8	0.40
5	<i>n</i> -Butanol	130	210	43	33	160	33.8	0.39
6	Cyclohexane	133	240	300	633	113	37.2	0.28
7	Toluene	135	250	700	900	153	37.4	0.37
8	Tetrahydrofuan	135	243	425	1000	170	36.3	0.41
9	Acetone	138	205	35	65	185	36.1	0.45

The bond strength calculations were performed using the Gaussian 98 suite of programs [14] with the density function model B3P86 (Becke 3 Perdew–Wang 86 (B3P86); [15a,b]) and the cc-pVDZ basis set [16]. The optimized geometries were obtained for the species, and single point energies were then computed using the polarized continuum model (PCM) [17] to account for solvent effects on the –O–O– bond dissociation energy (BDE).

The data show that significant decomposition DTB of 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, so the overall extent of reactive hazards for DTBP in each of these nine solvents appears to be comparable.

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

5. 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 hazard classification for thermal reactivity based on the onset temperature (T_{onset}) and the heat of reaction ($-\Delta H$) of a compound as shown in Fig. 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 chemicals in Class I.
4. Class IV: These chemicals react at higher temperatures and are mildly exothermic.

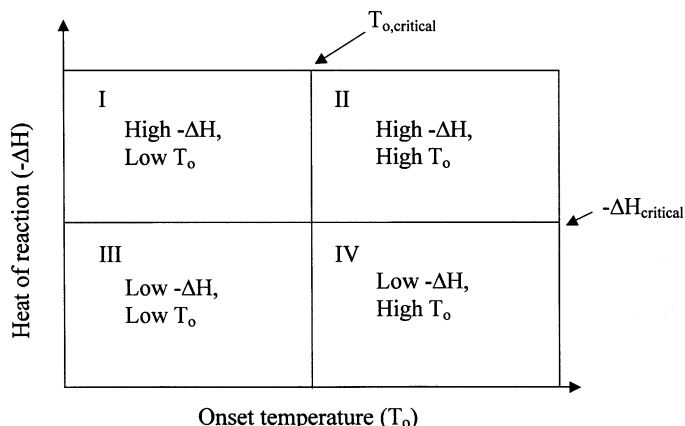


Fig. 3. Proposed thermal hazard classification for reactive chemicals.

Thus, reactive hazard decreases from Classes 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 chemicals 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, but chemicals in Classes III and IV pose medium and low hazard, respectively. This classification can be applied to storage, process, and transport or can be used as a screen for detonation, deflagration, and runaway potential to select certain chemicals or compositions for more detailed testing.

5.1. Choice of critical values

This hazard classification places fixed or rigid thresholds or boundaries based on the values of 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 static limits, the choice of threshold values is subject to judgment, and choices for these value are discussed below.

We recommend a value of 200 °C for the critical onset temperature $T_{\text{onset,critical}}$. This value is consistent with the NFPA intrinsic thermal stability rating [18], 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 (660 cal/g). The ASTM CHETAH program [19] calculates the maximum heat of decomposition from 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, 1.5 kJ/g (~ 350 cal/g) can be selected as a critical threshold value for the heat of reaction, $\Delta H_{\text{critical}}$. A critical review of CHETAH and certain other hazard evaluation systems by Melhem and Shanley is available [20].

Table 3
DSC data for various compounds [12]

Serial number	Compound	T_{onset} (°C)	Heat of reaction (cal/g)	Hazard rating
1	<i>p</i> -Nitrotoluene	366	372	High
2	3,5-Dinitrobenzoic acid	374	760	High
3	Trinitrotoluene	314	1287	High
4	Benzoyl peroxide	108	438	Very high
5	<i>t</i> -Butyl hydroperoxide	98	252	Medium
6	Cumene hydroperoxide	187	448	Very high
7	Xanthene	190	80	Medium
8	Benzyl chloride	172	269	Medium
9	2-Bromo- <i>n</i> -butyric acid	91	309	Medium

A plot of T_{onset} versus heat of reaction for DTBP in the nine solvents is shown in Fig. 4, which shows that all the compositions lie in Class III, as illustrated in Fig. 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. Onset temperatures measured in screening tests are often higher than those measured with more sophisticated or sensitive calorimeters at near-adiabatic conditions. Therefore, for higher operating temperatures that approach the onset temperatures measured at the screening level, additional tests to measure more accurate onset temperatures are recommended.

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 is recommended.

DSC 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_{onset} and displayed in Fig. 5.

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:

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

where the temperatures are in K. The lesser 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 rate. With

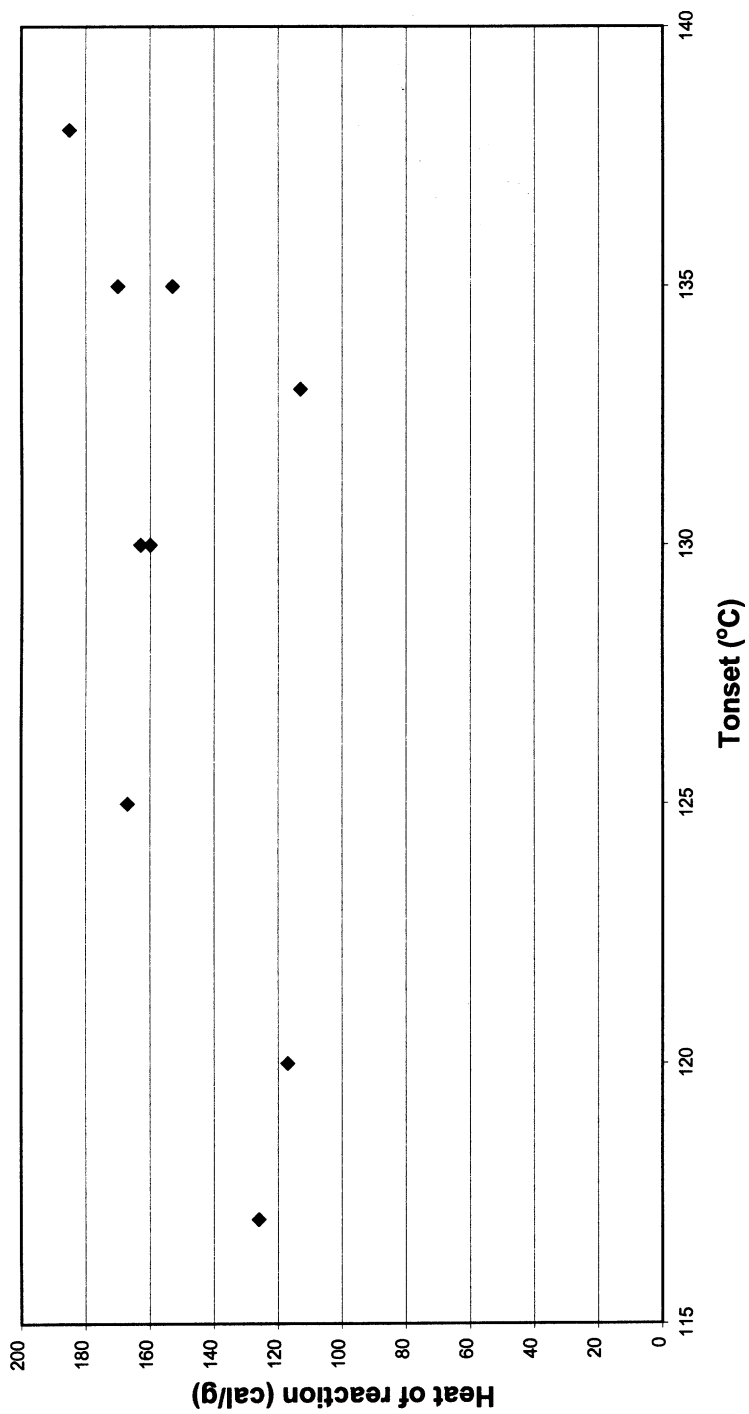


Fig. 4. Heat of reaction for DTBP in the nine solvents.

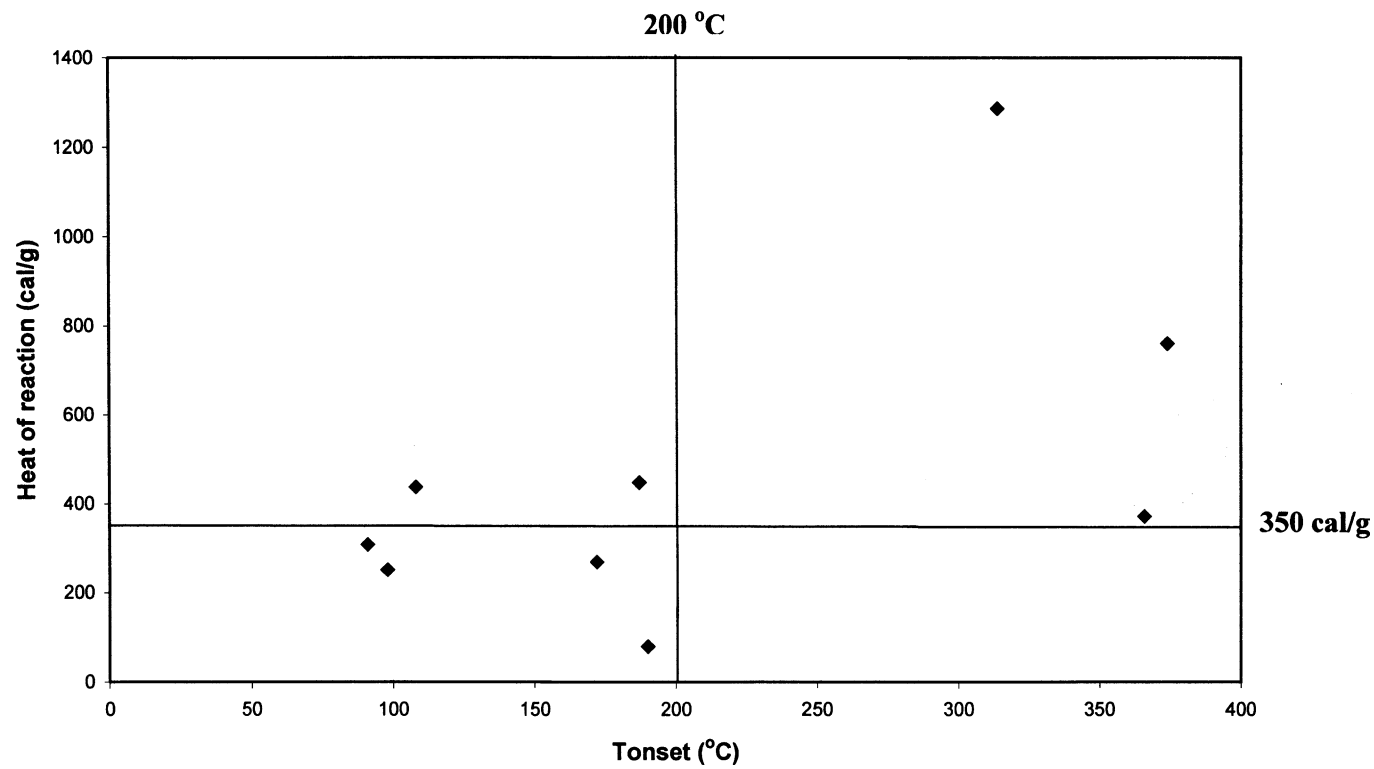


Fig. 5. Hazard classification of DSC calorimetric data for selected compounds [12].

increasing temperature, the rate of reaction increases in an exponential fashion according to the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

where k is the rate constant, A is the frequency factor, E_a is the activation energy, R is the gas constant (1.987 cal/mol 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.

$$\beta = -\frac{\Delta H}{350}$$

β is a thermodynamic quantity and is a measure of the energy release potential of a substance and a measure of the consequence of the reaction, whereas τ is a measure of probability of reaction occurrence. 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. This risk can be expressed quantitatively by defining a reactivity risk index (RRI), as follows:

$$\text{RRI} = \tau \times \beta = \left(\frac{T_{\text{process}}}{T_{\text{onset}}}\right) \times \left(-\frac{\Delta H}{350}\right)$$

The lower the value of the product, $\tau \times \beta$, the lower the risk due to a lower reactivity and/or lower energy released from the reaction of a substance. RRI values for 30 wt.% DTBP in the nine solvents at a process temperature of 75 °C (348 K) representing the relative risk of these nine DTBP solutions is included in Table 2.

6. Conclusions

The onset temperatures and heats of reaction for 30 wt.% DTBP in a variety of organic solvents were measured using a RSST, and the experimental values were compared with –O–O– bond strength calculations to estimate solvent effects on the –O–O– bond dissociation energies. Based on the measured overall reactivity, the reactive hazards of DTBP in the nine solvents are similar. The systems studied were a part of a larger effort at the MKOPSC to generate reactivity data for potentially hazardous chemicals and compositions. A hazard classification for thermal reactivity based on onset temperature and the energy released is recommended as a useful tool for reactive chemical hazard assessment. Also, a RRI, is defined for a chemical substance as a guide for reactivity risk comparisons.

Acknowledgements

The Gaussian computations were performed on the Texas A&M supercomputer, and we acknowledge the technical support of the TAMU supercomputing center. We thank Dr. J.P. Gupta for his valuable suggestions.

References

- [1] J.A. Barton, P.F. Nolan, Chem. E Symp. Ser. I 115 (1989) 3.
- [2] J.C. Etchells, Org. Process Res. Dev. 1 (1997) 435.
- [3] J.L. Gustin, Risk Anal. 12 (4) (1992) 475.
- [4] J. Barton, R. Rogers, Chemical Reaction Hazards, 2nd Edition, Institute of Chemical Engineers, UK, 1997.
- [5] <http://www.fauske.com>
- [6] <http://www.adlittle.com>
- [7] C.M. McClosekey, Plant Operation Prog. 8 (4) (1989) 185.
- [8] D.E. Clark, Chem. Health & Saf. 8 (2001) 12.
- [9] J.H. Raley, F.F. Rust, W.E. Vaughan, J. Am. Chem. Soc. 70 (1948) 1336.
- [10] E.S. Huyser, C.J. Bredweg, J. Am. Chem. Soc. 86 (1964) 2401.
- [11] T.C. Hoeflich, M.S. LaBarge, J. Loss Prev. Process Ind. 15 (2002) 163.
- [12] T. Ando, Y. Fujimoto, S. Morisaki, J. Hazard. Mater. 28 (3) (1991) 251.
- [13] D.I. Townsend, J.C. Tou, Thermochim. Acta 37 (1980) 1.
- [14] M.J. Frisch, G.W. Trucks, H.B. Schiegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98 (Revision A.9), Gaussian, Inc., Pittsburgh, PA, 1998.
- [15] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
(b) J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
- [16] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
- [17] S. Miertus, J. Tomasi, Chem. Phys. 65 (1982) 239.
- [18] NFPA 704, Standard system for the identification of the hazards of materials for emergency response, 2001.
- [19] CHETAHTM, Version 7.2, The ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation (NIST Special Database 16), ASTM Subcommittee E27.07, ASTM, West Conshohocken, PA, 1998.
- [20] G.A. Melhem, E.S. Shanley, Process Saf. Prog. 15 (3) (1996) 168.