

Thermal risk assessment and rankings for reaction hazards in process safety

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Abstract Reaction hazards remain the most serious concern in the chemical industry in spite of continual research and attention devoted to them. Many commercial calorimeters, such as the Differential Scanning Calorimetry (DSC), are useful screening tools for thermal risk assessment of reaction hazards. Some important thermodynamic and kinetic parameters, including onset temperature, adiabatic time to maximum rate, and maximum adiabatic temperature, were analyzed in this paper. A kinetic-based model under adiabatic conditions was developed, and the adiabatic time to maximum rate was estimated. Correlations between onset temperature (T_o) and activation energy (E_a), and between onset temperature (T_o) and adiabatic time to maximum rate (TMR_{ad}) were found, and were illustrated by some examples from the previous literature. Based on the heat of reaction and the adiabatic time to maximum rate, a thermal risk index (TRI) was defined to represent the thermal risk of a specific reaction hazard relative to di-*tert*-butyl peroxide (DTBP), and the results of this index were consistent with those of the reaction hazard index (RHI). The correlations and the thermal risk index method could be used as a preliminary thermal risk assessment for reaction hazards.

Keywords Thermal risk · Differential scanning calorimetry · Onset temperature · Adiabatic time to maximum rate · Reaction hazard index

List of symbols

A_0	Pre-exponential factor
BDE	Bond dissociation energy
C_A	Concentration (mol/m ³)
C_p	Specific heat capacity (J/kg·K)
C_{pc}	Specific heat capacity of container (J/kg·K)
C'_p	Specific heat capacity (J/mol·K)
DSC	Differential Scanning Calorimetry
DTBP	Di- <i>tert</i> -butyl peroxide
E_a	Activation energy (kJ/mol or kcal/mol)
h	Planck's constant (J·s)
$-\Delta H_r$	Heat of reaction (kJ/mol or cal/g)
k	Rate constant (1/s)
k_B	Boltzmann's constant (J/K)
m	Mass of chemical sample (kg)
m_c	Mass of container (kg)
\dot{q}	Heat release rate at any temperature (W/kg)
\dot{q}_o	Heat release rate at T_o (W/kg)
R	Gas constant (J/mol·K)
r_A	Reaction rate (mol/m ³ ·s)
RHI	Reaction hazard index
t	Time (s or min)
T	Absolute temperature (K)
TBPA	<i>t</i> -Butyl peroxy acetate
T_m	Maximum adiabatic decomposition temperature (K)
TMR_{ad}	Time to maximum rate at adiabatic conditions (s or min)
T_o	Onset temperature where the heat release rate is 0.1 °C/min (K)
TRI	Thermal risk index
V	Reaction volume (m ³)

Greek symbols

β	Ratio of consequence
γ_p	Transfer coefficient

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- ε Ratio of probability
 Φ Thermal inertia coefficient

Introduction

Thermal risk evaluation of reaction hazards is of great importance to the safer operation of chemical processes [1, 2]. The thermal reactivity or thermal instability [3, 4] of a compound is an inherent property of the compound and the characterization of the thermal reactivity is considered as a dynamic problem. Both thermodynamic and kinetic studies are necessary to evaluate the thermal risk. In previous research by Ando et al. [5], the onset temperature (T_o) and the heat of reaction ($-\Delta H_r$) are considered as two significant parameters to assess reaction hazards. It was suggested that thermal risk of chemical reactions could be characterized both by their severity and by their probability [6]. First, the severity of a chemical reaction has to be determined. Usually severity can be described by the heat of reaction or the adiabatic temperature rise [7]. If the process temperature is above the onset temperature, the time to maximum rate under adiabatic condition (TMR_{ad}) could be used to describe the probability of thermal risk [7, 8].

It is well known that to evaluate the thermal reactivity and to design a safe chemical process, all the thermodynamic and kinetic parameters, including onset temperature, adiabatic time to maximum rate and maximum adiabatic temperature must be determined. But a correct determination of the thermo-chemical kinetics for a reaction is time consuming and therefore, preliminary screening methods, such as the Differential Scanning Calorimetry (DSC), are usually applied in the chemical industry. DSC is regarded as a useful screening tool for thermal risk assessment and for the investigation of decomposition mechanisms of exothermic reactions [9, 10].

The purpose of this work is to demonstrate that a reasonable ranking of thermal risk is possible. The demonstration is based on a kinetic model and correlations between T_o and E_a , and between T_o and TMR_{ad} , which are derived from a limited number, 37 sets, of DSC data [5]. A new approach for assessing reaction hazards was also proposed and compared with a previous evaluation method of reaction hazards. We believe that the proposed ranking method of reaction hazards can be used to screen reaction hazards during chemical process designs.

Data collection

Exothermic onset temperatures (T_o) and heats of reaction ($-\Delta H_r$) were collected from a previously published

measurements in a pressure DSC (DU Pont 910 pressure-type) [5]. These experiments were performed with about 1–2 mg samples in an aluminum cell and a scanning rate of 10 °C/min for 820 reactive hazards of which 37 reactive hazards were chosen in this work. The data sets were selected on the basis of different functional groups for compounds undergo decomposition with a bond scission as the first reaction step. The decomposition of these types of compounds may be first order, which will help to obtain a reasonable model later. The concerned physical properties, such as molecular weight (MW) and specific heat capacity (C_p), are available from the National Institute of Standards and Technology [11]. For those experimental values that are unavailable in the literature or handbooks, Gaussian03 programs were used to estimate them with good accuracy. Specific heat capacity values (J/mol·K) were calculated using the quicker and less expensive semi-empirical AM1 method [12]. Both experimental and calculated data are displayed in Table 1.

Model development

In order to relate calorimetric data (T_o , $-\Delta H_r$) to activation energy and time to maximum rate, an unsteady state model in an adiabatic batch reactor was employed [13]. It has been shown that such a model can fairly well relate calorimetric data with activation energy and is based on the following assumptions [14]:

- The reaction system is assumed to be adiabatic, and therefore heat losses are negligible.
- The mass and volume of the liquid phase remain constant (i.e. evaporation losses are neglected). The specific heat of the liquid is considered to be constant during the reaction.
- A uniform temperature exists throughout the liquid phase.
- The decomposition reaction is first order with concentration, therefore

$$r_A = kC_A \quad (1)$$

With these assumptions, the following heat balance can be written

$$(-\Delta H_r)(-r_A)V + \Phi m C_p \frac{dT}{dt} = 0 \quad (2)$$

where ΔH_r is the heat of reaction (kJ/mol), r_A is the reaction rate (mol/m³·s), V is the reaction volume (m³), m and C_p are the mass (kg) and specific heat capacity (J/kg·K) of the chemical compound, respectively. Φ is the thermal inertia coefficient which is defined as

$$\Phi = \frac{mC_p + m_c C_{pc}}{mC_p} \quad (3)$$

Table 1 DSC data and physical property values for various compounds

Compound name	Molecular formula	Molecular weight (g/mol)	Heat capacity (J/mol·K)	Heat of reaction (cal/g)	Onset temperature (°C)
<i>Organic peroxides</i>					
Benzoyl peroxide	C ₁₄ H ₁₀ O ₄	242	243	438	108
<i>t</i> -butyl hydroperoxide	C ₄ H ₁₀ O ₂	90	123	252	98
Cumene hydroperoxide	C ₉ H ₁₂ O ₂	152	169	448	187
Dilauroyl peroxide	C ₂₄ H ₄₆ O ₄	399	387	232	86
Di- <i>tert</i> -butyl peroxide (DTBP)	C ₈ H ₁₈ O ₂	146	219	133	162
Methylethylketone peroxide	C ₈ H ₁₈ O ₆	210	220	345	99
<i>Nitro compounds</i>					
Nitrobenzene	C ₆ H ₅ NO ₂	123	186 ^a	312	400
2,4,6-Trinitrotoluene	C ₇ H ₅ N ₃ O ₆	227	243 ^a	1287	314
2-Nitroaniline	C ₆ H ₆ N ₂ O ₂	138	166 ^a	485	341
3-Nitroaniline	C ₆ H ₆ N ₂ O ₂	138	159 ^a	605	345
4-Nitroaniline	C ₆ H ₆ N ₂ O ₂	138	167 ^a	601	347
2-Nitrotoluene	C ₇ H ₇ NO ₂	137	172 ^a	317	338
3-Nitrotoluene	C ₇ H ₇ NO ₂	137	172 ^a	260	361
4-Nitrotoluene	C ₇ H ₇ NO ₂	137	172 ^a	372	366
<i>Oximes</i>					
Benzaldoxime	C ₇ H ₇ NO	121	126	410	236
Biacetylmonoxime	C ₄ H ₇ NO ₂	101	122	220	159
Cyclohexanoneoxime	C ₆ H ₁₁ NO	113	199 ^a	527	207
Dimethylglyoxime	C ₄ H ₈ N ₂ O ₂	116	142	455	254
<i>Azo compounds</i>					
Azobenzene	C ₁₂ H ₁₀ N ₂	182	229 ^a	191	321
Azoxybenzene	C ₁₂ H ₁₀ N ₂ O	198	185	405	307
<i>Epoxy compounds</i>					
2,3-Epoxy-1-propanol	C ₃ H ₆ O ₂	74	83	241	197
1,2-Epoxypropane	C ₃ H ₆ O	58	125 ^a	67	160
<i>Chlorides</i>					
Benzoyl chloride	C ₇ H ₅ ClO	141	187 ^a	481	190
Benzyl chloride	C ₇ H ₇ Cl	127	182	269	172
<i>o</i> -Chlorobenzoyl chloride	C ₇ H ₄ Cl ₂ O	175	125	865	164
2-Amino-4-chlorophenol	C ₆ H ₆ NCIO	144	134	48	164
2,6-Dichlorobenzoyl chloride	C ₇ H ₃ Cl ₃ O	209	140	694	229
2,4,5-Trichlorophenol	C ₆ H ₃ Cl ₃ O	197	141	699	268
1,3-Dichloropropane	C ₃ H ₆ Cl ₂	113	125 ^a	81	243
<i>N-oxides</i>					
Pyridine- <i>N</i> -oxide	C ₅ H ₅ NO	95	88	380	288
γ -picoline- <i>N</i> -oxide	C ₆ H ₇ NO	109	113	368	285
Picolinic acid <i>N</i> -oxide	C ₆ H ₅ NO ₃	139	130	307	224
Trimethylamine <i>N</i> -oxide	C ₃ H ₁₂ NO	75	98	213	202
<i>Hydrazine</i>					
Benzoylhydrazine	C ₇ H ₈ N ₂ O	136	144	259	260
1,2-Diformylhydrazine	C ₂ H ₄ N ₂ O ₂	88	99 ^a	304	234
2-Hydroxyethylhydrazine	C ₂ H ₈ N ₂ O	76	95	251	240
4-Nitrophenylhydrazine	C ₆ H ₇ N ₃ O ₂	153	151	432	178

^a Heat capacity data are from the open literature, other heat capacity data are calculated by Gaussian03 programs

where m_c and C_{pc} correspond to the mass (kg) and specific heat of the container (J/kg·K). The thermal inertia coefficient is one of the most important parameters to insure that the calorimeter matches as close as possible to the chemical process. For typical industrial reactors, Φ is larger than but close to 1. However, to simplify the kinetic model, $\Phi = 1$ will be chosen in this work, which is the worse case for a thermal runaway reaction. In this case of $\Phi = 1$, all of the thermal energy released by the decomposition reaction will increase the temperature of the reacting system and accelerate the reaction. Combining Eqs. 1 and 2

$$\frac{dT}{dt} = \frac{-\Delta H_r k C_A V}{\Phi m C_p} \quad (4)$$

with $C'_p = (m/C_A V)C_p$ (C'_p is specific heat of the sample in J/mol·K) and $\Phi = 1$, Eq. 4 can be simplified as

$$\frac{dT}{dt} = \frac{-\Delta H_r k}{C'_p} \quad (5)$$

According to Transition State Theory (TST), the rate constant k can be represented by

$$k = \frac{k_B T}{h} \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

where k_B is the Boltzmann's factor (J/K), h is Planck's constant (J·s), E_a is the activation energy (kJ/mol), T is the absolute temperature (K) and R is the gas constant (J/mol·K). Substituting Eq. 6 into 5

$$\frac{dT}{dt} = \frac{-\Delta H_r k_B T}{C'_p h} \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

If the temperature at which the gradient of temperature with time (dT/dt) increases at the specified rate of 0.1 °C/min is taken as the onset temperature, activation energy can be calculated from Eq. 7.

For a decomposition reaction with relative high activation energy, it has been shown that the adiabatic time to maximum rate (TMR_{ad}) can be approximated [15].

$$TMR_{ad} = \frac{C_p RT_o^2}{\dot{q} E_a} \quad (8)$$

where \dot{q} is the corresponding heat release rate (W/kg) at the temperature T , E_a is the activation energy (kJ/mol), and C_p is the specific heat of the reaction mass (J/kg·K). In this model the concentration decrease is neglected, so that the calculated TMR_{ad} is always shorter than the true adiabatic value and, thus, the difference is on the conservative side. The heat release rate is defined as

$$\dot{q} = (-\Delta H_r)(r_A V) \quad (9)$$

It is also possible to estimate the heat release rate at any temperature T

$$\dot{q} = \dot{q}_o \exp\left(\frac{E_a}{R} \left(\frac{1}{T_o} - \frac{1}{T}\right)\right) \quad (10)$$

where \dot{q}_o is the heat release rate (W/kg) at the onset temperature T_o . Therefore, the adiabatic time to maximum rate starting from the onset temperature can be estimated as

$$TMR_{ad} = \frac{C_p RT_o^2}{\dot{q}_o E_a} \quad (11)$$

Combining Eqs. 2, 9 and 10, the heat release rate is

$$\dot{q}_o = \frac{dT}{dt} C_p \quad (12)$$

Substituting Eq. 12 into 11

$$TMR_{ad} = \frac{RT_o^2}{(dT/dt) E_a} \quad (13)$$

For an onset temperature corresponding to $dT/dt = 0.1$ °C/min, the adiabatic time to maximum rate can be estimated from the onset temperature and the activation energy according to Eq. 13. It should be noted that the thermo-kinetic analysis mentioned above is at best approximate (especially for the calculation of TMR_{ad}). Therefore, the models do not apply in cases of multiple reactions (in a competitive consecutive reaction network) or catalysis reactions.

Results and discussion

Correlations

As pointed out above, if the temperature at $dT/dt = 0.1$ °C/min is taken as the onset temperature, both the activation energy and the adiabatic time to maximum rate can be estimated using Eqs. 7 and 13. All data of onset temperature, activation energy, and adiabatic time to maximum rate are summarized in Table 2.

Two correlations in Eqs. 14 and 15 were developed based on the training set of 37 reaction hazards. Equation 14 shows the correlation between the onset temperature and the activation energy with an R^2 value of 0.99. Figure 1 displays the onset temperature against the activation energy.

$$T_o = 2.4953E_a - 247.7 \quad (14)$$

The second correlation was based on the adiabatic time to maximum rate and the onset temperature, as shown below as Eq. 15

$$TMR_{ad} = 0.2088T_o + 61.885 \quad (15)$$

Table 2 Summary data of adiabatic time to maximum rate and activation energy

Compound name	Heat of reaction (cal/g)	Onset temperature (°C)	Adiabatic time to maximum rate (min)	Activation energy (kJ/mol)
Benzoyl peroxide	438	108	83	145
<i>t</i> -Butyl hydroperoxide	252	98	82	139
Cumene hydroperoxide	448	187	100	176
Dilauroyl peroxide	232	86	79	135
Di- <i>tert</i> -butyl peroxide	133	162	98	161
Methylethylketone peroxide	345	99	82	141
Nitrobenzene	312	400	147	256
2,4,6-Trinitrotoluene	1287	314	124	231
2-Nitroaniline	485	341	133	236
3-Nitroaniline	605	345	133	239
4-Nitroaniline	601	347	133	240
2-Nitrotoluene	317	338	133	233
3-Nitrotoluene	260	361	139	241
4-Nitrotoluene	372	366	139	245
Benzaldoxime	410	236	110	195
Biacetylmonoxime	220	159	96	162
Cyclohexanoneoxime	527	207	105	183
Dimethylglyoxime	455	254	114	202
Azobenzene	191	321	131	224
Azoxybenzene	405	307	125	223
2,3-Epoxy-1-propanol	241	197	103	177
1,2-Epoxypropane	67	160	100	156
Benzoyl chloride	481	190	101	177
Benzyl chloride	269	172	98	167
<i>o</i> -Chlorobenzoyl chloride	865	164	93	171
2-Amino-4-chlorophenol	48	164	100	160
2,6-Dichlorobenzoyl chloride	694	229	107	196
2,4,5-Trichlorophenol	699	268	115	212
1,3-Dichloropropane	81	243	116	191
Pyridine- <i>N</i> -oxide	380	288	121	216
γ -picoline- <i>N</i> -oxide	368	285	121	214
Picolinic acid <i>N</i> -oxide	307	224	108	190
Trimethylamine <i>N</i> -oxide	213	202	105	178
Benzoylhydrazine	259	260	117	202
1,2-Diformylhydrazine	304	234	111	193
2-Hydroxyethylhydrazine	251	240	113	194
4-Nitrophenylhydrazine	432	178	98	173

This correlation also has an R^2 value of 0.99. The detailed information of the time to maximum rate against the onset temperature is displayed in Fig. 2. These equations and figures indicate that three thermo-kinetic parameters, T_o , E_a , and TMR_{ad} , are closely related to each other. The onset temperature can be approximately described as proportional to the activation energy. The adiabatic time to maximum rate is also proportional to the onset temperature. Therefore, a specific reaction hazard with high activation energy in the

decomposition reaction will have relatively high onset temperature and the adiabatic time to maximum rate will be large, which means that the thermal risk of this reaction hazard is relatively lower.

According to Eqs. 14 and 15, if the activation energy is known or can be estimated, then the onset temperature and the adiabatic time to maximum rate can be estimated. It is possible that the activation energy be estimated based on certain assumptions:

- The reaction follows a radical mechanism.
- The first step is the dissociation of the weakest bond, and the remaining steps are relatively fast.

Thermal decomposition reactions of the nitro compounds [16, 17] or organic peroxides [18, 19] can be depicted as bond scission reactions.

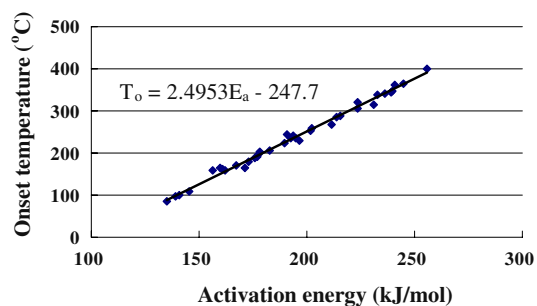


Fig. 1 A correlation between onset temperature and activation energy

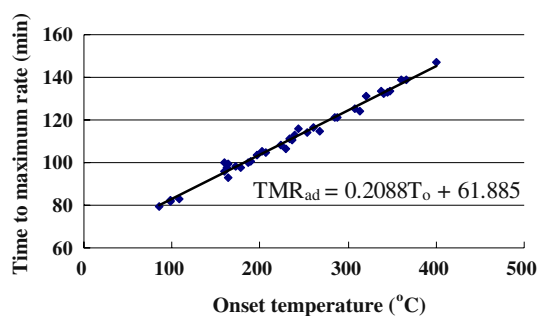


Fig. 2 A correlation between adiabatic time to maximum rate and onset temperature

Therefore, for these types of decomposition reactions (or any similar decomposition behaviors that have weakest bond broken), the bond scission reaction can be regarded as the rate-limiting step, and hence the activation energy can be estimated as [20]:

$$E_a = \gamma_p(\text{BDE}) \quad (18)$$

where γ_p is the positive transfer coefficient, BDE is the bond dissociation energy (kcal/mol) in the bond scission reaction, which can be calculated by Gaussian03 programs. The BDE data for some nitro compounds were collected from the published article by Saraf et al. [20], and shown in Table 3. The experimental activation energy of dicumyl peroxide [21], hydroxylamine [22], and *t*-butyl peroxy acetate (TBPA) [23] were obtained from the previous literature. The onset temperatures are then predicted according to Eq. 14. As seen from Table 3, the average error percentages are very small, and we can conclude that the predictions are reasonable and can be used to assess reaction hazards. The next section of this paper will show the thermal risk assessment of reaction hazards in detail.

Thermal risk evaluation

As we mentioned above, thermal risk is based on severity and probability. If these two parameters can be represented for a certain reaction hazard of chemical processes, thermal risk assessment of the reaction hazard is possible.

Severity and probability

The primary factors determining severities in chemical reactions are the energies that can be released in the reactions based on quantities of chemicals and the adiabatic temperature rise potentials. Typical decomposition thermal

Table 3 Summary of experimental and predicted values of onset temperature

Compound	Bond dissociate energy (kcal/mol)	Predicted activation energy (kJ/mol)	Onset temperature (°C)	Predicted onset temperature (°C)	Error (%)
2-Nitrotoluene	73.4	215	290	289	-0.4
3-Nitrotoluene	75.9	222	310	307	-1.0
4-Nitrotoluene	76.7	225	320	313	-2.2
2-Nitrobenzoic acid	66.4	194	270	238	-12.0
3-Nitrobenzoic acid	74.7	219	300	298	-0.6
4-Nitrobenzoic acid	76.5	224	310	311	0.4
2-Nitroaniline	80.1	235	280	338	20.6
3-Nitroaniline	76.5	224	300	311	3.8
4-Nitroaniline	80.9	237	310	344	10.8
Dicumyl peroxide	-	147 ^a	109	119	9.3
Hydroxylamine	-	160 ^a	139	152	9.0
TBPA	-	163 ^a	160	159	-0.6

^a Experimental values are from the previous literature

energies can lead to massive destruction even if they are only partially transformed into mechanical forms in a thermal runaway incident. Secondary effects, such as the release of toxic compounds, can significantly contribute to the overall degree of the severity. However, in this work we will not focus on toxic effects. Therefore, the heat of reaction, which is a measure of the energy release potential of a compound, will be used as a measure of the severity of the reaction [7].

Probabilities of thermal runaway reactions are more difficult to evaluate. However, it is reasonable to consider their immediate consequences by referring to time scales of runaway scenarios, or the adiabatic time to maximum rate starting from the onset temperature. It is obviously that a failure mode that triggers a severe runaway reaction within a few minutes following the onset temperature is dangerous. Therefore, the adiabatic time to maximum rate will be used to represent the probability of runaway reaction occurrence [8].

Thermal risk index (TRI)

In order to assess quantitatively a specific reactive hazard, it is necessary to define two parameters related to severity and probability. Di-*tert*-butyl peroxide (DTBP) is an extensively studied chemical [24] for its thermally unstable and simple unimolecular first-order decomposition reaction in the gas phase [25]. Therefore, DTBP is selected in this work as a reference compound to standardize the thermal risk index. The heat of reaction, $-\Delta H_r = 133$ cal/g, and the adiabatic time to maximum rate, $TMR_{ad} = 98$ min, for DTBP is used to define two dimensionless parameters and then estimate thermal reactivity risk. A ratio, β , as the amount of energy released by a specific substance to the energy released by DTBP is defined

$$\beta = \frac{-\Delta H_r}{133} \quad (19)$$

β is measurement of the severity of the reaction. The higher the value of β , more severe the chemical reaction is relative to the decomposition reaction of DTBP.

We can also define another ratio, ε , as the adiabatic time to maximum rate of DTBP to that of the substance.

$$\varepsilon = \frac{98}{TMR_{ad}} \quad (20)$$

ε is measurement of probability of reaction occurrence. The smaller the value of ε , the safer the process is, because there is more time to make adjustments to avert a runaway reaction or to reduce the consequences.

Because risk is the function of severity and probability [26], it may be expressed by these two parameters (although there are some other factors that may contribute to the risk):

$$\text{Risk} = \text{Severity} \times \text{Probability} \quad (21)$$

Combining definitions (19), (20), and (21), the thermal risk of a specific substance relative to DTBP can be represented quantitatively by defining a thermal risk index (TRI) as follows

$$TRI = \beta \times \varepsilon = \left(\frac{-\Delta H_r}{133} \right) \times \left(\frac{98}{TMR_{ad}} \right) \quad (22)$$

The lower the value of TRI, the lower the thermal risk is due to a lower reactivity. The thermal risk index values for all 37 compounds are calculated according to Eq. 22 and shown in Table 4. In this work, we assign thermal risk ranking values according to the rules as follows:

- 1 for $TRI < 1$;
- 2 for $1 \leq TRI < 2$;
- 3 for $2 \leq TRI < 3$;
- 4 for $TRI \geq 3$

Therefore, thermal risk rankings for all 37 reaction hazards are assigned and summarized in Table 4.

Reaction hazard index (RHI)

D. R. Stull has developed a ranking system, which is called the reaction hazard index (RHI), to establish the relative potential hazards of specific reactive chemicals [27]. The RHI relates the maximum adiabatic temperature (T_m) to the activation energy (E_a) of a decomposition reaction and is defined as

$$RHI = \frac{10T_m}{T_m + 30E_a} \quad (23)$$

where E_a is the activation energy (kcal/mol), and T_m is the maximum adiabatic decomposition temperature (K), which can be estimate as

$$T_m = T_o + \frac{-\Delta H_r}{C'_p} \quad (24)$$

where T_o is the onset temperature (K), C'_p is the specific heat of the sample (J/mol·K), and ΔH_r is the heat of reaction (kJ/mol).

The reaction hazard index values for all 37 reaction hazards are calculated and included in Table 4. The reaction hazard index relationship has a low value ($RHI < 4$) for relative low reactivity and high value ($RHI > 6$) for high reactivity. In this work, RHI rankings are assigned according to the rules as follows:

- 1 for $RHI < 4$;
- 2 for $4 \leq RHI < 5$;
- 3 for $5 \leq RHI < 6$;
- 4 for $RHI \geq 6$

Table 4 Results of TRI and RHI rankings

Compound name	Thermal risk index		Reaction hazard index		Overall ranking
	TRI value	Ranking	RHI value	Ranking	
Benzoyl peroxide	3.89	4	6.79	4	High
<i>t</i> -Butyl hydroperoxide	2.25	3	5.35	3	Medium
Cumene hydroperoxide	3.30	4	6.30	4	High
Dilauroyl peroxide	2.15	3	5.84	3	Medium
Di- <i>tert</i> -butyl peroxide	1.00	2	4.12	2	Medium
Methylethylketone peroxide	3.12	4	6.34	4	High
Nitrobenzene	1.56	2	4.56	2	Medium
2,4,6-Trinitrotoluene	7.65	4	7.72	4	High
2-Nitroaniline	2.70	3	5.76	3	Medium
3-Nitroaniline	3.36	4	6.22	4	High
4-Nitroaniline	3.32	4	6.11	4	High
2-Nitrotoluene	1.75	2	5.00	2	Medium
3-Nitrotoluene	1.38	2	4.65	2	Medium
4-Nitrotoluene	1.97	2	5.17	3	Medium
Benzaldoxime	2.74	3	6.07	4	High
Biacetylmonoxime	1.69	2	5.07	3	Medium
Cyclohexanoneoxime	3.70	4	5.69	3	High
Dimethylglyoxime	2.93	3	5.90	3	Medium
Azobenzene	1.07	2	4.34	2	Medium
Azoxybenzene	2.38	3	5.99	3	Medium
2,3-Epoxy-1-propanol	1.72	2	5.18	3	Medium
1,2-Epoxypropane	0.49	1	3.35	1	Low
Benzoyl chloride	3.52	4	6.10	4	High
Benzyl chloride	2.01	3	5.06	3	Medium
<i>o</i> -Chlorobenzoyl chloride	6.87	4	8.18	4	High
2-Amino-4-chlorophenol	0.36	1	3.63	1	Low
2,6-Dichlorobenzoyl chloride	4.79	4	7.75	4	High
2,4,5-Trichlorophenol	4.48	4	7.53	4	High
1,3-Dichloropropane	0.51	1	3.76	1	Low
Pyridine- <i>N</i> -oxide	2.31	3	5.96	3	Medium
γ -picoline- <i>N</i> -oxide	2.24	3	5.71	3	Medium
Picolinic acid <i>N</i> -oxide	2.09	3	5.79	3	Medium
Trimethylamine <i>N</i> -oxide	1.49	2	4.75	2	Medium
Benzoylhydrazine	1.64	2	5.18	3	Medium
1,2-Diformylhydrazine	2.02	3	5.42	3	Medium
2-Hydroxyethylhydrazine	1.64	2	4.93	2	Medium
4-Nitrophenylhydrazine	3.25	4	6.48	4	High

Based on two ranking methods (TRI and RHI), overall rankings in low, medium and high are also provided in Table 4. The methods of TRI and RHI are consistent with each other and are useful for the preliminary thermal risk assessment of reaction hazards. However, we would like to stress here that the methods of TRI and RHI are only for giving a general and global classification, and experimental tests are necessary to obtain the further accurate information of chemical reactivity.

Conclusions

The thermal reaction hazards can be evaluated through the aid of calorimetry with related models. In this work, the kinetic model under adiabatic conditions for the first order reaction was developed and two simple correlations among onset temperature, adiabatic time to maximum rate, and activation energy were presented. The correlations relate the main characteristics of the decomposition reactions

with acceptable accuracy. If the activation energy is known or can be estimated, the onset temperature and the adiabatic time to maximum rate can be estimated. Both the heat of reaction and the adiabatic time to maximum rate can then be used to evaluate potential reaction hazards. To represent the thermal risk for a chemical substance, a method of thermal risk index (TRI) was defined by product of severity and probability relative to DTBP. Reaction hazard index (RHI) values were also calculated based on activation energy and maximum adiabatic temperature. The final ranking results of these two methods are consistent with each other. The analysis presented in this work has potential applications in process safety, loss prevention, and emergency response for thermally sensitive hazards.

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