Thermal risk assessment and grading of chemicals with instantaneous power density

Daoxing Sun · Chuanxin Xie · Fan Zhang · Jing Gu · Jie Sun

Abstract The heat release behaviors of several chemical compounds were detected with C80 calorimeter. Furthermore, the thermodynamic and kinetic parameters of the chemicals were obtained based on the experimental data. Chemical thermal risk was simultaneously graded with combined use of instantaneous power density and the classification standard of thermal instability which was offered by the standard system for the identification of the hazards of materials for emergency response (NFPA704). The results show that the grading standard of thermal risk based on NFPA704 was reasonable and can be used as a preliminary thermal risk assessment for reaction hazards.

Keywords C80 calorimeter · Instantaneous power density · Thermal risk · Risk assessment and prevention

List of symbols

C_0	Initial reaction rate of reactant
Rate	Reaction rate of reactant (g mL^{-1} s^{-1})
M_0	Initial mass of reactant
M	Mass of reactant at time t
A	Pre-exponential factor of Arrhenius equation (s^{-1})
E_a	Activation energy (kJ mol^{-1})
ΔH	Reaction heat of unit reactant (kJ mol^{-1})
q_G	Heat release (kJ mol^{-1})
t	Reaction time (min)

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T	Temperature of system at time t (K)
$T_{o,s}$	Onset exothermic temperature
n	Reaction order
k	Constant of reaction rate
R	Gas constant (8.31415 J mol^{-1} K^{-1})
dH/dt	Overall heat flow (W)
dT/dt	Self-heat rate (K s^{-1})

Introduction

With rapid development of the chemical industry and the petroleum chemical industry, the production or use of flammable, explosive, toxic, harmful, corrosive dangerous chemicals are widely increased, and various safety accidents occurred frequently [1–5].

Reaction heat per unit mass (ΔH) refers to the difference between the heat formation of reaction products and reactants, by multiplying the amount of reactants, total reaction heat can be obtained. In an exothermic reaction, the larger the ΔH is, the more reaction heat release will be. In this case, the accumulated heat will be more and the risk will be greater. So, for the rapid chemical reactions, ΔH can predict the risk of chemicals or their mixtures to a certain extent. Benson groups adding principle can give danger level of chemical compounds based on the calculated reaction heat of exothermic reaction [6, 7].

However, reaction heat is calculated by the integral of the heat release during the whole reaction process. In other words, reaction heat only characterizes the energy change without involving the reaction time. So, although the reaction heats of different chemicals are similar, the degrees of violence and harm of the reactions are different due to their different reaction time, the factors of amount

and rate of heat lease must be therefore involved when discussing heat release. Thermal risk evaluation of reaction hazards is of great importance to the safer operation of chemical processes [8–10]. The thermal reactivity or thermal instability of a compound is an inherent property of the compound, and the characterization of the thermal reactivity is considered as a dynamic problem [11–14]. Both thermodynamic and kinetic studies are necessary to evaluate the thermal risk.

National Fire Protection Association (NFPA) of America presented the concept of instantaneous power density (IPD) by combining thermodynamics and kinetics. IPD is used to determine the thermal instability level of chemicals and comprehensively characterizes the dangerous degree of heat release during the reaction process.

The purpose of this study is to determine the rationality of NFPA704 about the grading standard of thermal hazardous chemicals based on the IPD parameter. We believe that the ranking method of reaction hazards can be used for the assessment and prevention of chemical accidents.

Experimental

Materials

Tert-Butyl peroxybenzoate (TBPB), industrial products, was purchased from Sinopec Qilu Petrochemical Corporation Group; 30% H_2O_2 was obtained from Tianjin Sanhe Chemical Company, China; NH_4NO_3 (analytical pure, AR) was received from Chengdu Kelong Chemical Factory, China; Epichlorohydrin (ECH), cyclohexanone, and ethyl propionate (AR) were obtained from Tianjin Bode Chemical Co., Ltd, China.

Experimental instruments

C80 calorimeter (SETARAM, France) which testing temperature range from room temperature to 300 °C is connected to a data acquisition and control unit, as well as to a computer equipped with the SETSOFT software, which can be used to calculate thermodynamics and kinetic data. Its structure sketch is shown in Fig. 1.

Experimental methods

Moderate amount of a sample was placed into the measurement cell, and the inert material (Al_2O_3) with the same weight of the sample was put into the reference cell. And then the measurement cell and reference cell were put into C80 calorimeter. Heating was carried out in the air atmosphere, and the heating rate was set according to the property of sample. Control software of C80 calorimeter
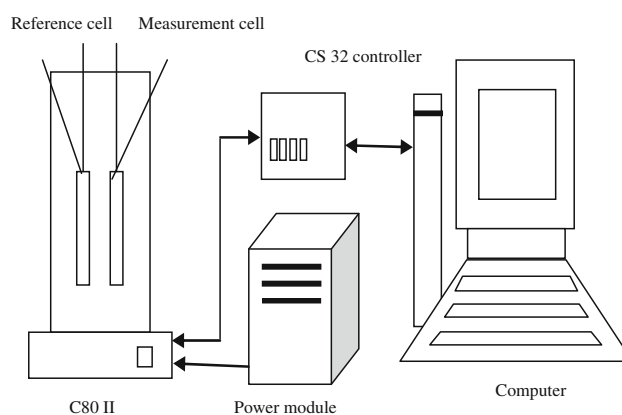

Fig. 1 Schematic diagram of C80 calorimeter

was used to observe the reaction process until end of the reaction.

Basic principles

IPD [15] is one of the important criteria to characterize the heat release rate per unit mass and the primary way to determine the degree of thermal hazard of chemicals. It synthetically characterizes the dangerous degree of heat release during the reaction process from the view of thermodynamics and kinetics.

The calculation equations of IPD are as follows:

$$IPD = -\Delta H \times Rate \tag{1}$$

$$IPD = -\Delta H \times C_0^n A \exp(-E_a/RT) \tag{2}$$

where rate is reaction rate, C_0 is the initial reaction concentration of the reactant, A, E_a, and R are pre-exponential factor (s^{-1}), Activation energy (kJ mol^{-1}), and gas constant (8.31415 J mol^{-1} K^{-1}) of Arrhenius formula, respectively. The degree of thermal instability hazards for chemicals (NFPA704 [16–18]) was divided into five levels from level 0 to 4 according to the energy releasing rates during chemical reactions. Level 0 is the most stable level, and level 4 is the most dangerous and highly explosive. IPD at the presumed temperature of 250 °C was used to determine the degree of thermal instability hazards of chemicals. Detailed classification method was shown in Table 1.

C80 is a heat flow micro calorimeter used to determine the heat flux produced from samples under isotherm or scanning mode. It has the reputation of high sensitivity and can measure heat effect of chemicals, physical process, and thermo-physical properties such as specific heat capacity and coefficient of heat conduction by setting different test procedures. Kinetic and thermodynamic parameters of chemical reaction process were obtained by the experimental data of C80 calorimeter based on the above

Table 1 Degrees of thermal instability hazards

Degrees of thermal instability	IPD/W mL^{-1} at 250 °C (482 °F)
4—Materials which are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures	IPD ≥ 1000
3—Materials that can detonate or explode but require a strong initiating source, or must be heated under confinement before initiation, or react explosively with water	100 ≤ IPD < 1000
2—Materials that are normally unstable and readily undergo violent chemical changes but do not detonate; also materials that may react violently with water	10 ≤ IPD < 100
1—Materials that are normally stable, but can become unstable at high temperature and pressures, or may react with water with some release of energy	0.01 ≤ IPD < 10
0—Materials that are normally stable even under fire explosive conditions, and that are not reactive with water	IPD < 0.01

mentioned method, and then IPD was calculated. Finally, degree of thermal instability of chemicals was determined by IPD.

Results and discussion

Reaction heat

If the heat release of per unit mass of a reactant is ΔH, the heat release rate is equal to the consumption rate of reactants; heat release is obtained by the integral of the amount and ΔH of reactants within the whole reaction temperature range [19, 20].

$$q_G = -\frac{\mathrm{d}H}{\mathrm{d}t} = \Delta H M^n A \exp(-E_a/RT) \tag{3}$$

where q_G is heat release (kJ mol^{-1}) of the reactant, dH/dt is overall heat flow (W), and M is initial mass of reactant. According to the above analysis, the heat release of chemical compounds can be calculated by the integral of heat flow curve within the range of reaction time and then the heat release per unit mass of reactants was obtained. Reaction heats of reactants obtained by C80 calorimeter were given in Table 2.

Reaction rate

The calculation formulas of IPD involve the kinetic parameters such as activation energy and pre-exponential

Table 2 ΔH of sample measured by C80 calorimeter

Sample	ΔH/J g^{-1}
TBPB	−761.8
30% H$_2$O$_2$	−772
ECH	−1308
Ethyl propionate	−18
NH$_4$NO$_3$	−2643.5
Cyclohexanone	−60

factor. It is crucial to calculate the kinetics parameters of chemical reaction by experimental data of C80 calorimeter.

Activation energy and pre-exponential factor

According to the theories of chemical reaction and Arrhenius law, reaction rate and consumption of reactants in the initial stage were so small that the mass of sample was considered to be constant. The equations (Eqs. 4–6) of reaction rate were deduced and simplified to describe the relations of heat release rate of chemicals [21].

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \Delta H M_0 A \exp(-E_a/RT) \tag{4}$$

$$\frac{\mathrm{d}H/\mathrm{d}t}{\Delta H M_0} = A \exp(-E_a/RT) \tag{5}$$

$$\ln\left(\frac{\mathrm{d}H/\mathrm{d}t}{\Delta H M_0}\right) = \ln A - \frac{E_a}{RT} \tag{6}$$

The heat flow in the initial stage of reaction obtained by C80 calorimeter corresponded with Eq. 4. The data of heat flow was substituted into Eq. 5, and $\ln\left(\frac{\mathrm{d}H/\mathrm{d}t}{\Delta H M_0}\right)$ versus $\frac{1}{T}$ diagrammatic curve was drawn. Straight line was obtained by linear regression of $\ln\left(\frac{\mathrm{d}H/\mathrm{d}t}{\Delta H M_0}\right)$ versus $\frac{1}{T}$ diagrammatic curve. Activation energy and pre-exponential factor were obtained according to the slope and ordinate at the origin of the regression straight.

Figure 2 is the heat flow curve of ECH measured by C80 calorimeter with the mass of 1.00 g sample and the heating rate of 0.20 °C min^{-1}. It can be seen from Fig. 2 that ECH started to release heat at the temperature of 175 °C and the strong exothermic peak appeared at 200 and 250 °C, respectively.

The correlative curve of ECH of $\ln\left(\frac{\mathrm{d}H/\mathrm{d}t}{\Delta H M_0}\right)$ versus $\frac{1}{T}$ from Eqs. 4 and 5 was shown in Fig. 3. Figure 3 shows that $-\frac{E_a}{R} = -21341.47$ and $\ln A = 36.09$, so E_a and A are equal
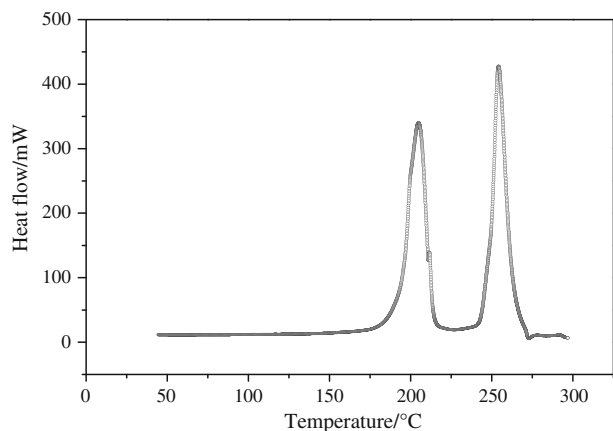
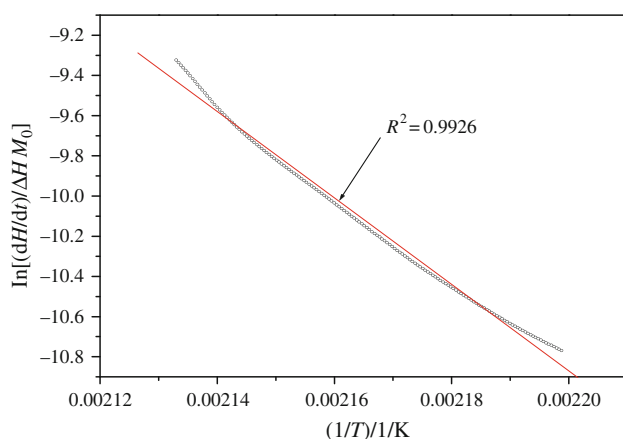Fig. 2 Heat flow curve of ECH measured by C80 calorimeter

Fig. 3 The correlative curve of $\ln[(dH/dt)/(\Delta HM_0)]$ and $(1/T)$

to 177.43 kJ mol^{-1} and 4.73×10^{15} s^{-1}, respectively. A and E_a value of the other reactants can be obtained in the same way.

Reaction order

A, E_a, and ΔH in definite temperature ranges are constant and heat flow can be measured by experiment for the same

chemical. Thus, reaction order can be determined by the reasonable setting procedure and conditions of experiments [22–25]. Heat flow curve of different chemical compounds at the fixed temperature was obtained by changing the dosage of chemicals and keeping the experimental temperature constant. Equations 7–10 were obtained on the basis of measured data of heat flow were substituted into Eq. 3.

$$\left(\frac{dH}{dt}\right)_1 = \Delta H(M_{01})^n A \exp(-E_a/RT) \qquad (7)$$

$$\left(\frac{dH}{dt}\right)_2 = \Delta H(M_{02})^n A \exp(-E_a/RT) \qquad (8)$$

$$\frac{(dH/dt)_1}{(dH/dt)_2} = \left(\frac{M_{01}}{M_{02}}\right)^n \qquad (9)$$

$$n = \frac{\ln(dH/dt)_1 - \ln(dH/dt)_2}{\ln(M_{01}) - \ln(M_{02})} \qquad (10)$$

Reaction order can be calculated by Eq. 10 and the experimental data of different initial dosage of chemicals at the same temperature.

IPD

According to the above methods and experimental data measured by C80 calorimeter, A, E_a, and n can be determined. IPD at the temperature of 250 °C was calculated by the Eq. 2. The risk degree (Table 3) was determined based on IPD at the temperature of 250 °C and NFPA704.

It can be seen from Table 3 that under the same experiment condition, chemicals with high ΔH are more dangerous only by comparing the heat release per unit mass. However, the results are different when both the reaction heat and rate are considered. For example, when only ΔH is compared, ECH is more dangerous than TBPB for the measured ΔH of ECH (-1308 J g^{-1}) is larger than that (-761.8 J g^{-1}) of TBPB. However, the reaction of TBPB is more violent than that of ECH, because the reaction rate (5.18×10^4 g mL^{-1} s^{-1}) of TBPB at the temperature of 250 °C is larger than that (1.06×10^{-2} g mL^{-1} s^{-1}) of ECH. It comes to the conclusion that the IPD of TBPB and ECH at the temperature of

Table 3 Degrees of thermal instability hazards of sample

Sample	TBPB	30%H$_2$O$_2$	NH$_4$NO$_3$	ECH	Ethyl propionate	Cyclohexanone
ΔH/J g^{-1}	-761.8	-772	-2643.5	-1308	-18	-60
E_a/kJ mol^{-1}	192.06	104.00	353.67	177.43	164.80	15.30
A/s^{-1}	7.59×10^{23}	3.12×10^{11}	1.74×10^{34}	4.73×10^{15}	1.10×10^{16}	2.90×10^{-2}
Rate$_{523K}$/g mL^{-1} s^{-1}	5.18×10^4	14.10	1.42×10^{-1}	1.06×10^{-2}	3.36×10^{-1}	8.20×10^{-4}
IPD/W mL^{-1}	3.95×10^7	1.09×10^4	375.38	13.86	6.05	4.92×10^{-2}
Dangerous degree	4	4	3	2	1	1

250 °C are 3.95×10^7 W mL^{-1} and 13.86 W mL^{-1}, and their grade of thermal instability hazard are level 4 and 2, respectively, so TBPB is more dangerous than ECH. The hazard degree of energy release during the reaction can be characterized correctly by IPD which combines both kinetic and thermodynamic parameters of chemical reaction.

Conclusions

The grading standard of degrees of thermal instability hazards (NFPA704) effectively combined the reaction heat and rate and reflects heat release behaviors of chemicals with acceptable accuracy based on the choice of IPD as characterization parameter. It can provide technical support for evaluation and prevention of chemical accidents. The kinetic and thermodynamic parameters were determined, and then IPD was calculated based on the experimental data measured by C80 calorimeter and related theories. According to the standard grade of thermal instability hazards, IPD was used to determine the hazard level of chemicals which is consistent with the real risk of chemicals. This approach provides a high reference value to evaluate thermal hazard of chemicals.

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