

Runaway reaction of lauroyl peroxide with nitric acid by DSC

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Abstract Pooling lauroyl peroxide (LPO) with nitric acid, we used differential scanning calorimetry (DSC) to assess the thermokinetic parameters, such as exothermic onset temperature (T_0), heat of decomposition (ΔH_d), frequency factor (A), and the other safety parameters. When LPO was contaminated with nitric acid (HNO_3), we found the exploder 1-nitrododecane. Obvious products were sensitive and hazardous chemicals. Concentration reaching 1–12 N HNO_3 emitted a large amount of heat. This study combined with curve-fitting method to elucidate its unsafe characteristics and thermally sensitive structure to help

prevent runaway reactions, fires and explosions in the process environment. According to the findings and the concept of inherently safer design, LPO runaway reactions could be adequately prevented in the relevant plants.

Keywords Curve-fitting method · Differential scanning calorimetry · Thermokinetic parameters · Lauroyl peroxide · Runaway reactions

List of symbols

A	Frequency factor ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)
C_p	Heat capacity ($\text{J g}^{-1} \text{K}^{-1}$)
E_a	Activation energy (kJ mol^{-1})
ΔH_d	Heat of decomposition (J g^{-1})
m	Total mass of reactant (g)
n	Reaction order (dimensionless)
P	Pressure (psig)
P_{\max}	Maximum pressure (psig)
Q	Total heat of decomposition (kJ kg^{-1})
Q_t	Decomposition heat released at time t (kJ kg^{-1})
Q_1^∞	Heat effect of the stage (dimensionless)
R	Gas constant ($8.31415 \text{ J k}^{-1} \text{ mol}^{-1}$)
r_1	Reaction rate of first stage (g s^{-1})
r_2	Reaction rate of second stage (g s^{-1})
SADT	Self-accelerating decomposition temperature ($^\circ\text{C}$)
T	Absolute temperature ($^\circ\text{C}$)
ΔT_{ad}	Adiabatic temperature rise ($^\circ\text{C}$)
T_{\max}	Temperature at which the peak point occurs ($^\circ\text{C}$)
TMR	Time to maximum rate (day)
T_{NR}	Temperature of no return ($^\circ\text{C}$)
T_0	Exothermic onset temperature ($^\circ\text{C}$)
U	Heat transfer coefficient ($\text{kJ min}^{-1} \text{m}^{-2} \text{K}^{-1}$)
α_i	Degree of conversion (dimensionless)
β	Heating rate ($^\circ\text{C min}^{-1}$)

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Introduction

Many accidents are caused by thermal runaway reactions [1, 2]. One of the most famous was a disastrous release of a large volume of methyl isocyanate gas from a Union Carbide plant in Bhopal, India, in December 1984 [3]. Thermal runaway occurs when the reaction rate increases due to an increase in temperature, causing a follow up increase in pressure and hence a further increase in the reaction rate. Thermal runaway is also a concern in hydrocracking, an oil refining process [4]. In the chemical industry, many production processes involve exothermic reactions. Thermal runaway may result from exothermic side reactions that begin at higher temperatures, followed by an initial accidental overheating of the reaction mixture. Understanding of runaway reactions is necessary to predict and govern hazards. A detailed kinetic modeling approach is proposed to simulate runaway reactions under process conditions.

Organic peroxides are characterized by the presence of a sensitive oxygen–oxygen bond. Especially, contact with acids, alkalis, heavy metals, reducing agent, and any rust should be avoided. Shock, friction, fire or other sources of ignition should be also avoided during a manufacturing process [5–8]. Many thermal explosion incidents caused by organic peroxide have occurred in Taiwan [9]. In practice lauroyl peroxide (LPO) [4, 10] is one of the typical organic peroxides. In our studies, runaway reactions of LPO with HNO_3 involve a highly exothermic peak that could induce a thermal accident and damage the process equipment and the surroundings. It is very important to make clear the safety parameters and reaction situation for LPO mixing with contaminant.

Kotoyori [11] establishes a self-accelerating decomposition theoretical model, the self-accelerating decomposition temperature (SADT) of LPO as approximately 48 °C. Due to hazardous consequences of decomposition of LPO with acids and its extensive use in the industry, we have made an effort to understand the runaway reaction phenomenon by evaluating the kinetic parameters.

Safety parameters must be taken into account for evaluating the degree of hazard based on the thermokinetic parameters, such as exothermic onset temperature (T_0), activation energy (E_a), frequency factor (A), etc. The decomposition of LPO with HNO_3 produces a strong exothermic peak belonging to an n th order reaction. This study has proposed a method to generalize the concept of runaway reaction regarding LPO with HNO_3 by employing differential scanning calorimetry (DSC) as a quantitative measure of reactivity, allowing one to take proper account of kinetic complexity. On the basis of the curve-fitting method and experimental results, we found that a quickly appearing exothermic peak indicated its dangerous features. Therefore,

to prevent accidents from occurring, thermal hazard information should be provided to plant personnel in order to alleviate the degree of hazard, and also to the process engineers to design a safer control system, such as the cooling system, alarm system, interlock system, etc. [12].

Application of safety parameters

Safety is the most important element during storage or transport of chemicals, so safety parameters must be precisely evaluated. Then one can decide whether a cooling system should be established or not. These chemicals are stored in a container that could be exposed to a thermal source, self-decomposition, or unexpected mixing with contaminants to prompt runaway reactions, such as fire or explosion. In the absence of proper controls, a serious accident could thus be triggered during the upset situations.

According to the methodologies proposed by Townsend and Tou [13] and Fisher and Goetz [14], important safety parameters, such as time to maximum rate (TMR), temperature of no return (T_{NR}), and SADT, could be employed to evaluate the degree of hazard to reduce an unacceptable contingency. The results obtained are suitable for the study of the phenomenon of runaway reactions involving pure substances or mixtures. These safety parameters are described below.

TMR

LPO with HNO_3 has a highly exothermic peak during the decomposition reaction; therefore, TMR is an adequate indicator to study the variation between time and temperature in four different heating rates (1, 2, 4, and 10 °C min^{-1}).

The calculation method by Townsend and Tou is shown in Eqs. 1 and 2 [10]:

$$\text{TMR} = \frac{RT^2}{AE_a\Delta T_{\text{ad}}} e^{-E_a/RT} \quad (1)$$

$$\Delta T_{\text{ad}} = \frac{Q}{C_p} \quad (2)$$

Thermokinetic parameters via experimental results belong to n th order reaction and only have one exothermic peak for appropriating this method.

T_{NR}

During an upset situation a suitable and deliverable emergency response must be adopted. T_{NR} is an important index in common use, which could be calculated via the relationship between the rates of heat generation and heat removal [15]. It could be applied to design a cooling

system and to inform fire fighters about the remaining time to conduct a rescue operation [16], because T_{NR} increases with the temperature of runaway reaction. T_{NR} can be computed by Eqs. 3 and 4 given below:

$$(T_{NR} + 273.15)^2 = \frac{mE_a\Delta Hk}{RU(1.8)a} \quad (3)$$

$$= \frac{mE_a\Delta HAe^{-E_a/R(T_{NR} + 273.15)}}{RU(1.8)a} \quad (4)$$

SADT

SADT is extensively employed to estimate the decomposition reaction of thermally unstable materials, such as the O–O bond of organic peroxide, which is defined as the minimum ambient air temperature at which a self-reactive substance of specified stability (contaminant level, inhibitor concentration, vessel volume filled ratio, etc.) undergoes an exothermic reaction in a specified commercial package in a period of 7 days or less. A self-reactive substance must be subject to temperature control, inhibitor, improving the materials, and volume for a container during transportation if its SADT is less than or equal to 50 °C [17, 18]. Equation 5 could be used to calculate this safety parameter:

$$\text{SADT} = T_{NR} - \frac{R(T_{NR} + 273.15)^2}{E_a} \quad (5)$$

Experimental setup

Sample preparation

Ninety five mass% LPO was purchased directly from the Fluka Co., and then stored in a refrigerator at 4 °C. Four types of inorganic acids were selected to combine with LPO for studying its incompatible reactions—1, 2, 6, and 12 N HNO₃—as the contaminants of interest. The original concentration of HNO₃ was 65 mass%, and then distilled water was used as the thinner for allocating the above-mentioned concentrations. HNO₃ was obtained from Hayashi Pure Chemical Ind., Co., Ltd. in Japan. The mixture reactions were stirred at room temperature and then put into the device for testing.

DSC

Temperature-programmed screening experiments were performed (Mettler TA8000 system) and coupled with a measuring cell that could withstand relatively high pressure to approximate 100 bar (DSC 821^e). STAR^e software was used to obtain thermal curves. DSC has been calibrated with regard to both heat flux and temperature. For better

thermal equilibrium, the scanning rate chosen for the temperature-programmed ramp was 4 °C min⁻¹. The range of temperature rise was chosen from 30 to 300 °C for each condition of experiments. This apparatus could properly acquire the heat flow, and then via experimental data to calculate the T_0 , T_{max} , and ΔH_d in the interior function of DSC [19]. Processing of experimental data and kinetic evaluation were implemented by applying TDPro and Fork software developed by CISP Ltd. [20].

Results

Different concentrations of HNO₃ were used as the contaminants, mixed with 95 mass% LPO for DSC. The experimental results are displayed in Tables 1 and 2 and Figs. 1, 2, 3. In the investigation, mixing with contaminant acids showed a strong phenomenon. 12 N HNO₃ caused a high degree of hazard during the experiments. In the thermal decomposition process we newly found the detonation product 1-nitrododecane. In the 12 N nitric acid contamination even more thermal energy was emitted.

Discussion

Curve-fitting analyses based upon experimental data

Thermokinetic parameters can be established by selecting an appropriate kinetic model to identify its basic characteristics as given in Eqs. 6–10. Curve-fitting reflected similar data as the experimental data.

The model for decomposition of LPO 95 mass% has only one stage:



The following mathematical model describes an n th order reaction:

$$r = \frac{d\alpha}{dt} = k_1(T)f \quad (7)$$

$$f = (1 - \alpha)^n \quad (8)$$

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}(1 - \alpha)^n \quad n\text{th order reaction} \quad (9)$$

$$\frac{dQ}{dt} = Q_i^\infty r_i \quad (10)$$

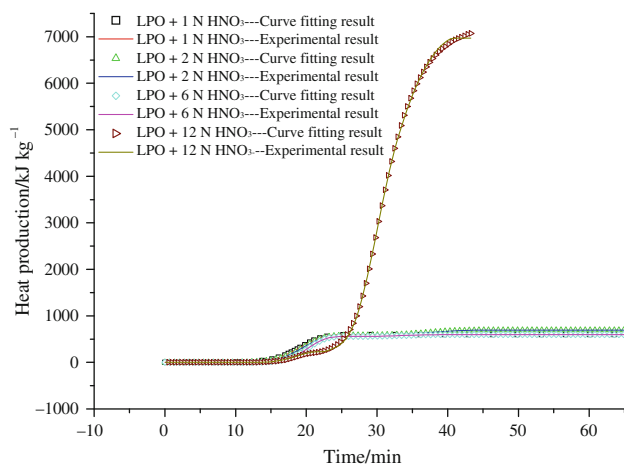
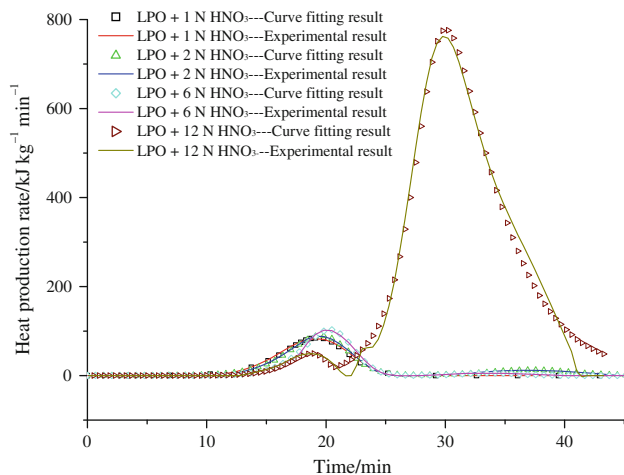
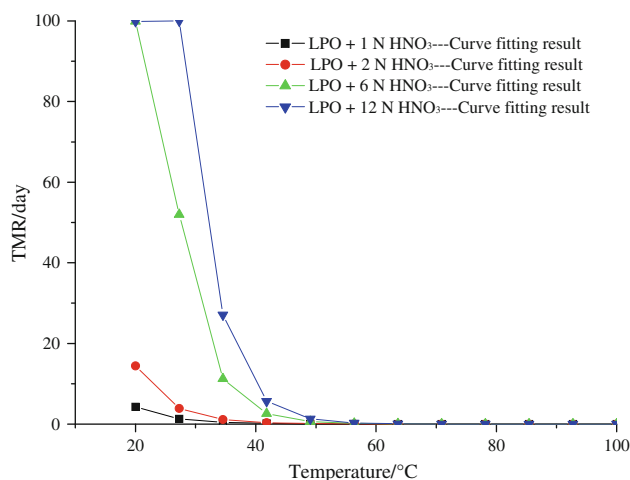
where α is the degree of conversion, r and Q_i^∞ denote reaction rate and heat effect of the stage, respectively; dQ/dt is the overall heat generating rate; f denotes kinetic function for the stage that depends on the extent of conversion; $k_i(T)$ obeys the Arrhenius temperature dependency of the rate constant: $k_i(T) = A \exp(-E_a/RT)$; A and E_a

Table 1 Thermokinetic parameters derived from the DSC data sets on LPO with HNO₃ for the first peak of the reaction

Sample	<i>m</i> /mg	β /°C min ⁻¹	E_a /kJ mol ⁻¹	<i>n</i>	ln(<i>A</i>)/ln(s ⁻¹)	ΔH_d /J g ⁻¹
LPO + 1 N HNO ₃	10.90	4	124.05	1.28	34.19	599.59
LPO + 2 N HNO ₃	7.51	4	137.59	1.29	38.45	582.09
LPO + 6 N HNO ₃	5.37	4	167.51	1.29	47.66	560.22
LPO + 12 N HNO ₃	6.07	4	178.84	0.76	52.31	177.51

Table 2 Thermokinetic parameters derived from the DSC data sets on LPO with HNO₃ for the second peak of the reaction

Sample	<i>m</i> /mg	β /°C min ⁻¹	E_a /kJ mol ⁻¹	<i>n</i>	ln(<i>A</i>)/ln(s ⁻¹)	ΔH_d /J g ⁻¹
LPO + 2 N HNO ₃	7.51	4	160.72	1.61	37.71	112.24
LPO + 6 N HNO ₃	5.37	4	200.91	1.67	50.36	37.62
LPO + 12 N HNO ₃	6.07	4	165.47	2.44	1.42	7093.72

**Fig. 1** Fitting of experimental data sets on heat production for LPO with 1, 2, 6, and 12 N HNO₃**Fig. 2** Fitting of experimental data sets on heat production rate for LPO with 1, 2, 6, and 12 N HNO₃**Fig. 3** TMR vs. temperature (kinetics-based simulation) for LPO with 1, 2, 6, and 12 N HNO₃

represent, respectively, the frequency factor and the activation energy of the stage; R is the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

After the thermokinetic parameters were evaluated by curve-fitting from the above model, all the data indicated that the decomposition of LPO with acids was dangerous reaction, because in the temperature range of 30–300 °C, its activation energy (E_a) was ca. 124–178 and 160–200 kJ mol⁻¹ in the conditions of LPO mixed with 1, 2, 6, and 12 N HNO₃ for the first and second peak, respectively. All the values of E_a were less than 220 kJ mol⁻¹. To precisely acquire the thermokinetic parameters, such as E_a , frequency factor (A), reaction order (n), and heat of decomposition (ΔH_d), it was important to have a good base line to integrate the exothermic peak for each of the thermal curves.

In thermal analysis for loss prevention, safety parameters are the important index for classifying the degree of hazard for LPO with HNO_3 . Hazardous characteristics of LPO and the effect of HNO_3 can be determined by comparing TMR. Figure 3 displays the TMR of temperature calculated on the basis of the kinetic models. TMR is treated as a measure of probability of runaway development if an accident occurs. The temperature range was set at 20–100 °C; LPO mixed with HNO_3 was most likely to trigger a runaway. When temperature was higher than 40 °C, TMR was approached in less than a day. Since LPO with HNO_3 had two exothermic reactions, SADT and T_{NR} could not be calculated by mathematical model directly. HNO_3 must be well separated while one is dealing with LPO in the manufacturing process.

Conclusions

This study focused on LPO with specific inorganic acids, here HNO_3 , for testing the specific reactive hazard. The characteristic hazardous runaway reaction relationship was explored for LPO with four different concentrations by using experimental and curve-fitting methods. LPO with acids was unstable due to its thermally reactive structure and hence cannot be used without sound safety systems. According to the experimental results, LPO is very sensitive to inorganic acids, especially at high concentrations 12 N. The degree of hazard increases significantly if the temperature and contaminants are not well dictated. Therefore, for prevention of LPO accidents, the safety information discussed in this paper must be brought to the notice of all the relevant plants. It is important to separate storage as that can reduce personal injury and damage caused in case of fires, spills or leaks. LPO should be kept away from incompatible materials such as strong acids and bases, other oxidizing materials, flammable or combustible liquids.

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