# Effect of inorganic salt and organic acid on the thermal runaway of hydrogen peroxide

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**Abstract:** Hydrogen peroxide with the presence of catalytic metal ions or incompatible organic matters has caused some fire and explosion accidents in recent years. This work further studied the effect of inorganic salt and organic acid on the thermal runaway behaviour of hydrogen peroxide via rapid screening device (RSD), accelerating rate calorimeter (ARC) and a batch reactor. Experimental results revealed that both the metal ions and their corresponding inorganic acid ions have significant influences on the thermal runaway of $H_2O_2$: the catalytic effect of metal ion followed $Fe^{2+} > Fe^{3+} > Cu^{2+}$, and the synergistic effect of inorganic acid ion followed $Cl^- > SO_4^{2-}$. No explosion was detected under RSD and ARC test conditions. In addition, a one-step global reaction kinetic model characterized as adiabatic temperature increase and final exothermic temperature was briefly described to estimate the kinetic parameters of the mixture of $H_2O_2$ with/without organic acid. The analysis showed that the runaway reaction of $H_2O_2$ with formic acid or acetic acid is a first order reaction at a low temperature range (< 100 °C) and the thermal runaway risk of $H_2O_2$/HCOOH > $H_2O_2$/$CH_3$COOH, along with the decreasing apparent activation energy and pre-exponential factor.

**Keywords:** hydrogen peroxide; runaway reaction; inorganic salt; organic acid; RSD; ARC

## Nomenclature

| | |
|---|---|
| $A$ | pre-exponential factor, 1/s |
| $c_v$ | specific heat, kJ/kg-K |
| $E_a$ | apparent activation energy, kJ/mol |
| $k$ | reaction rate constant, 1/s |
| $m$ | mass, kg |
| $n$ | reaction order |
| $P$ | pressure, MPa |
| $q$ | specific reaction heat, kJ/kg |
| $Q$ | total reaction heat, kJ |
| $r$ | temperature rise rate, °C/min |
| $r_T$ | self-heat rate, °C/min |
| $R$ | ideal gas constant, J/mol-K |
| $t$ | time, s |
| $T$ | temperature, K |
| $\Delta T_{ad}$ | adiabatic temperature increase, K |

Subscripts

| | |
|---|---|
| 0 | initial |
| c | control |
| exo | exothermic |
| f | final |
| L | liquid |
| max | maximum |

## 1. Introduction

Hydrogen peroxide ($H_2O_2$), as a multi-functional green oxidizing agent, is widely used in chemical synthesis of different peroxides, oil desulphurization, environmental protection and wastewater treatment, etc., owing to its environmentally friendly physico-chemical properties. In general, the normal decomposition rate of commercially supplied $H_2O_2$ is extremely low, under 1% loss per year (Mackenzie, 1990). However, the violently exothermic reaction of hydrogen peroxide mixed with incompatible contaminations has been well known, including metal ions and other organic matters. Some fatal fire and explosion accidents of $H_2O_2$ in recent years have been summarized in the previous work (Wu et al., 2011&2018).

Recently, the thermal risk of $H_2O_2$ or other organic peroxides have been experimentally studied via differential scanning calorimetry (DSC) (Liu et al., 2015; Chi et al., 2012; Grahamm et al., 2011; Wu et al., 2009 & 2010;), accelerating rate calorimeter (ARC) (Liu et al., 2010) and glass vessel (Eto et al., 2009) or Dewar flask (Eissen et al., 2003), Phi-TEC II adiabatic calorimeter and Thermal screening unit (Vianello et al., 2015&2018; Reyes Valdes et al., 2016; Casson et al.,2012; McIntosh et al., 2003), RC1e (Zhang et al., 2016), as well as other vessel test apparatuses (Papadaki et al., 2005; Kumasaki et al., 2006; Raines et al., 2006; Ni et al., 2016; Wu et al., 2018). Kinetic parameters are of importance for better understanding of the thermal runaway mechanisms, which has been also investigated with some theoretical models. Lu et al. (2006) determined the criteria of critical runaway of hydrogen peroxide with hydrochloric acid and estimated the kinetic parameters of decomposition reaction by using a reactive system screening tool (RSST) apparatus. Liu et al. (2010) investigated the effect of $Fe^{3+}$ on thermal explosion of hydrogen peroxide and found that the presence of $Fe^{3+}$ leads to a lower apparent activation energy ($E_a$) and a higher pre-exponential factor ($A$). Gómez et al. (2017) theoretically assessed the catalytic decomposition of hydrogen peroxide with two dimensionless characteristic parameters: adiabatic temperature rise and Damköhler number. Wu et al. (2018) assessed the explosion risk of hydrogen peroxide with presence of $Fe^{3+}$, organic acid and other organic matters such as acetone and ethanol in a pressurized batch reactor. They (Wu et al., 2018) found that the mechanism to trigger the thermal runaway of $H_2O_2$ is different between the metal ions and organic matters, i.e., explosions were observed in the mixture of $H_2O_2$ and organic matters only. Moreover, the kinetic parameters of $H_2O_2$ with $Fe^{3+}$ were studied based on a modified adiabatic theoretical model. However, neither the runaway reaction mechanism of the mixture of $H_2O_2$ and organic acids, nor the impact of inorganic salts on $H_2O_2$ decomposition has been well studied.

This work aims to improve the understanding of the thermal runaway behaviours of $H_2O_2$ with inorganic salt and organic acid. First, we experimentally studied the thermal characteristics of $H_2O_2$ under the contaminations of inorganic salt and organic acid via rapid screening device (RSD). By varying the volume and type of metal ion or organic acid, we determined the proportion between $H_2O_2$ and impurities at the worst scenario condition. Second, the mixture of $H_2O_2$ and formic or acetic acid at the worst scenario condition were further investigated by ARC, and then the kinetic parameters were estimated based on a one-step adiabatic reaction model. As a result, the effect of inorganic salt and organic acid on the thermal runaway of hydrogen peroxide were estimated experimentally and theoretically.

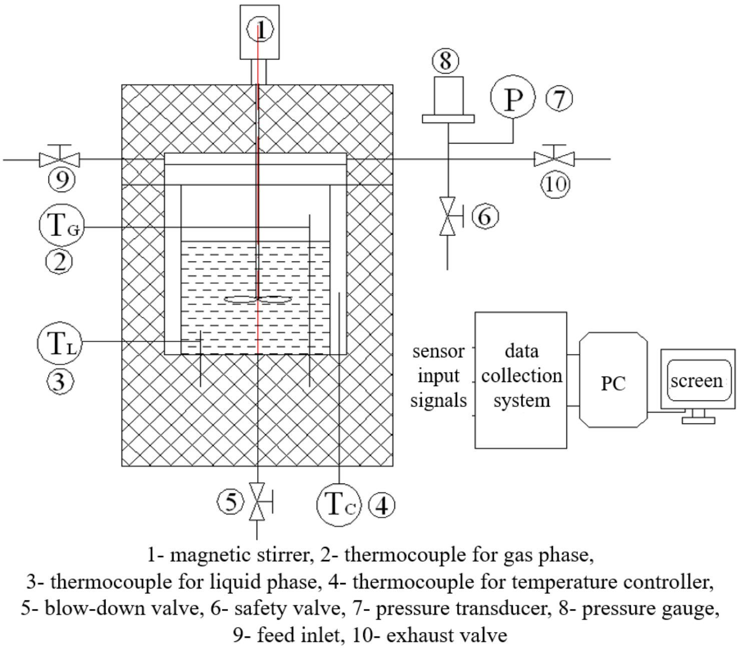
## 2. Experimental apparatus and procedure

### *2.1 Experimental samples*

30% $H_2O_2$ (mass fraction, hereinafter the same) was selected as the reagent in this work. Considering the previous accidents of $H_2O_2$, $Fe^{3+}$, $Fe^{2+}$ and $Cu^{2+}$ ions are typical metal impurity, thus ferric sulphate $Fe_2(SO_4)_3$ (≥99.0%), $FeSO_4·7H_2O$ (≥99.0%), $FeCl_3·6H_2O$ (≥99.0%) and $CuSO_4·5H_2O$ (≥99.0%) were selected. Formic acid and acetic acid as catalysts were widely used with the $H_2O_2$ on the oxidative desulphurization (Filippis et al., 2002), thus we chose formic acid HCOOH (≥88.0%) and acetic acid (≥99.5%) as the organic impurities in this work. All the experimental samples were purchased from Beijing Chemical Reagent Co., Ltd.

### *2.2 Experimental methods*

Both calorimeter and batch reactor tests were adopted to determine the thermal runaway behaviours of hydrogen peroxide in this work. RSD and ARC made by Thermal Hazard Technology Co. were used. The desired mass of $H_2O_2$ sample with or without impurities was placed in the titanium bomb chamber, sealed in air atmospheres for both RSD and ARC tests. RSD test was used for fast thermal hazard assessment to decide if the further thermal assessment is necessary. The sample was heated until 300 °C with a constant heating rate of 5 °C/min. Similar with ARC test procedure described in Liu et al. (2010), the placed sample was initially heated to 25 °C, and then equilibrated for 30 min, followed by a 15 min seeking for an exothermic signal with a slope sensitivity of 0.02 °C/min. If no exothermic signal was detected (i.e., self-heat rate <0.02 °C/min), then the temperature was increased by 4 °C with the subsequent repetition of the heat-wait-seek (H-W-S) mode. This mode continued until to an exothermic signal was detected. An extra test was conducted in our previous developed batch reactor as shown in Fig. 1. The details of the experimental apparatus and the experimental procedure were given in Wu et al. (2018).



1- magnetic stirrer, 2- thermocouple for gas phase,
3- thermocouple for liquid phase, 4- thermocouple for temperature controller,
5- blow-down valve, 6- safety valve, 7- pressure transducer, 8- pressure gauge,
9- feed inlet, 10- exhaust valve

**Fig. 1.** The schematic diagram of the batch reactor.

## 3. Experimental results and discussion

### *3.1 The impact of inorganic salt*

The details of the RSD test results of $H_2O_2$ with different types and mass fractions of metal ion are summarised in Table 1. Figure 2 shows the effect of $CuSO_4$ concentration on the temperature and the pressure evolutions of $H_2O_2$ conducted by RSD apparatus. $T_c$ is the system temperature controlled by RSD apparatus. It reveals that the initial exothermic temperature ($T_{0,\text{ exo}}$) which was defined by Waldram et al. (2002) as an onset temperature decreases by around 30 °C as $CuSO_4$ content increases from 0% to 2.25% by weight, suggesting a strong concentration effect. But this concentration effect on the peak pressure of the system is small since the peak pressure per mass maintains at around 2.2 MPa/g for all four samples as shown in Fig. 2b. Consequently, the catalytic effect of $Fe^{3+}$ promotes the decomposition reaction rate of hydrogen peroxide, while it has a limited effect to trigger an explosion. This result is consistent with our previous observation that no explosion was detected of $H_2O_2$ with a metal ion through a batch reactor (Wu et al., 2018). In addition, both the temperature and the pressure of the mixture of $H_2O_2$ and $CuSO_4$ decrease dramatically after reaching the peak value, which may result from the complete depletion of $H_2O_2$ and the heat loss to through the wall of the sample bomb chamber.

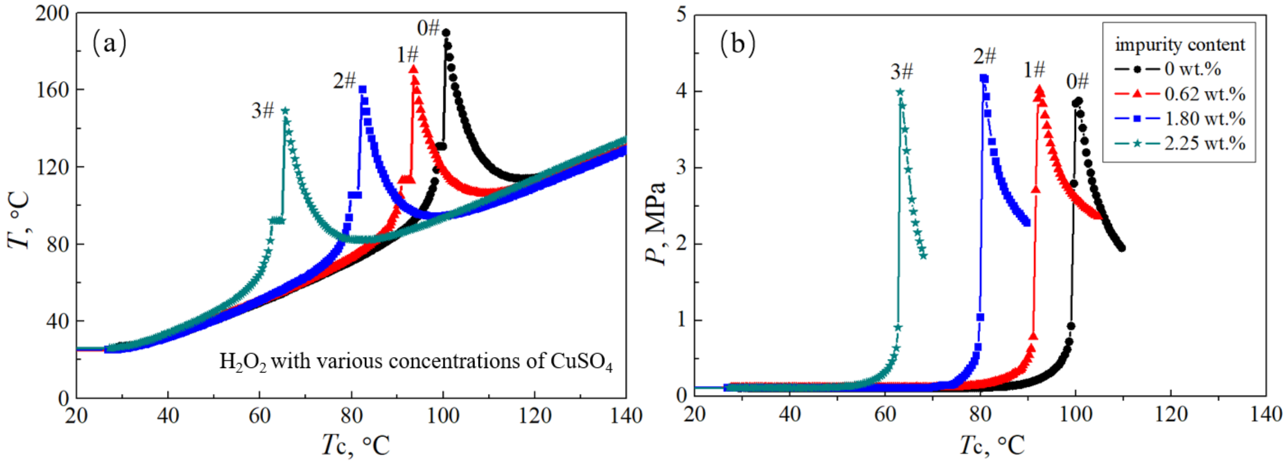


**Fig. 2.** Evolution of $H_2O_2$ with various concentrations of $CuSO_4$ in RSD test: (a) *T* and (b) *P*.

Similar with $Cu^{2+}$ ion, the presence of $Fe^{3+}$ ion promotes the decomposition of $H_2O_2$, decreasing the thermal stability of $H_2O_2$ as shown in Fig. 3. The higher content of $Fe^{3+}$ ion, the lower the initial exothermic temperature of $H_2O_2$ is: $T_{0,\text{ exo}}$ decreases by around 30 °C as $Fe^{3+}$ ion content increases from 0.60% to 2.38% by weight. The details of the initial exothermic temperature or onset temperature are listed in Table 1. The peak pressure per mass is around 2.3 MPa/g shown in Fig. 3b, which is slightly higher than that of $CuSO_4$. To further study the catalytic activity of different metal ions on the thermal runaway reaction of $H_2O_2$, an extra test was carried out by using our developed batch reactor. The revolution of the liquid temperature and the pressure for 200 mL $H_2O_2$ with various inorganic salts is illustrated in Fig. 4. The results reveal that 0.004 mol $Fe^{2+}$ has the highest catalytic activity on the decomposition of $H_2O_2$ since it reaches the maximum temperature firstly, while 0.004 mol $Cu^{2+}$ has the lowest catalytic activity, i.e., the thermal risk of $H_2O_2$ with the presence of metal ions follows $Fe^{2+} > Fe^{3+} > Cu^{2+}$. In general, catalytic mechanism of metal ions on the decomposition of $H_2O_2$

follows the well-known Haber-Weiss reaction (Koppenol, 2001). Moreover, the corresponding inorganic acid ion also significantly influences the catalytic activity of metal ion. Even 0.001 mol $Fe^{3+}$ ion with $Cl^-$ ion has a much stronger catalytic effect on both the temperature and the pressure of $H_2O_2$ thermal runaway than 0.004 mol $Fe^{3+}$ ion with $SO_4^{2-}$ ion. This means that the synergistic effect of inorganic acid ion follows $Cl^- > SO_4^{2-}$.

**Table 1** Measured results for $H_2O_2$ with different types and mass fractions of metal ion in RSD test.

| sample | mass/g | $Cu^{2+}$ (0.1 mol/L) mass fraction | $Fe^{3+}$ (0.1 mol/L) mass fraction | $T_{0,\,exo}$/°C | $T_{max}$/°C | $P_{max}$/MPa |
|---|---|---|---|---|---|---|
| 0# $H_2O_2$ | 1.90 | 0 | - | 77.4 | 189.7 | 3.9 |
| 1# $H_2O_2$ | 1.77 | 0.62 | - | 67.0 | 170.2 | 4.0 |
| 2# $H_2O_2$ | 1.80 | 1.80 | - | 61.9 | 160.4 | 4.2 |
| 3# $H_2O_2$ | 1.91 | 2.25 | - | 46.8 | 148.9 | 4.0 |
| 4# $H_2O_2$ | 1.81 | - | 0.60 | 64.0 | 158.5 | 4.3 |
| 5# $H_2O_2$ | 1.86 | - | 1.17 | 60.8 | 167.5 | 4.2 |
| 6# $H_2O_2$ | 1.90 | - | 1.71 | 46.4 | 165.8 | 4.7 |
| 7# $H_2O_2$ | 1.81 | - | 2.38 | 35.5 | 178.8 | 3.9 |

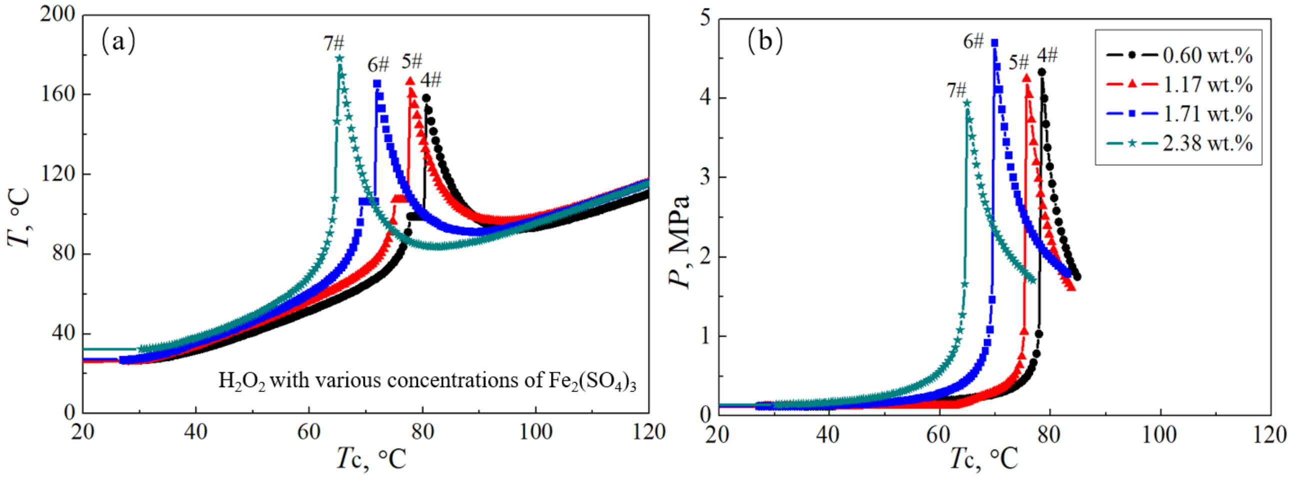


**Fig. 3.** Evolution of $H_2O_2$ with various concentrations of $Fe_2(SO_4)_3$ in RSD test: (a) $T$ and (b) $P$.

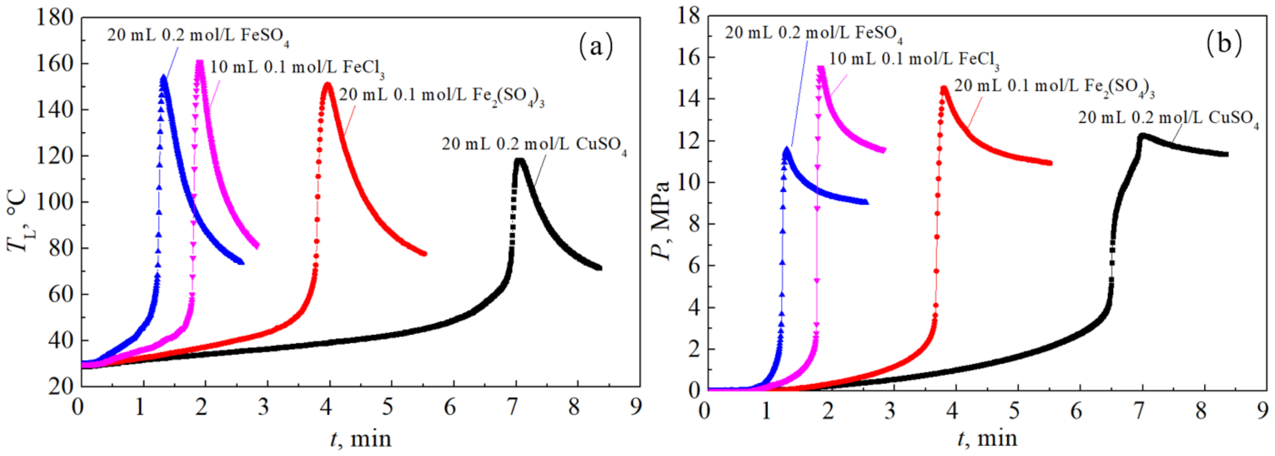


**Fig. 4.** Evolution of 200 mL $H_2O_2$ with various metal ions in the batch reactor at $T_0$ of 25 °C: (a) $T_L$ and (b) $P$.

### *3.2 The impact of organic acid*

Figure 5 illustrates the evolution of the mixture of $H_2O_2$ with various contents of HCOOH in RSD test. It shows that as the volume ratio of $H_2O_2$/HCOOH decreases from 3 to 1, the initial exothermic temperature ($T_{0, exo}$) significantly decreases from 75.5 °C to 41.7 °C, the maximum temperature ($T_{max}$) slightly decreases and the peak pressure ($P_{max}$) fluctuates.  When the volume ratio of $H_2O_2$/HCOOH decreases to 0.5, $T_{0, exo}$ even reduces to the ambient room temperature (around 25 °C), thus the information of its temperature and pressure evolution was failed to determine in this case. Overall, it is difficult to determine the best volume ratio of $H_2O_2$/HCOOH that would lead to the worst thermal runaway scenario. Compared with the mixture of $H_2O_2$/HCOOH, the mixture of $H_2O_2$/$CH_3COOH$ starts the exothermic reaction at a higher temperature region as shown in Fig. 6. As the volume ratio of $H_2O_2$/$CH_3COOH$ decreases from 2 to 0.5, $T_{0, exo}$ decreases, and both of $T_{max}$ and $P_{max}$ reach their maximum values when the volume ratio of $H_2O_2$/$CH_3COOH$ is 1, suggesting that the worst scenario occurs when the volume ratio of $H_2O_2$/$CH_3COOH$ equals 1. Nevertheless, the reaction reactivity of HCOOH and $CH_3COOH$ with $H_2O_2$ is still not well studied. Thus, the advanced ARC test was conducted afterwards. For simplicity, the volume ratio of $H_2O_2$/organic acid was selected as 1 for the convenience of comparison.

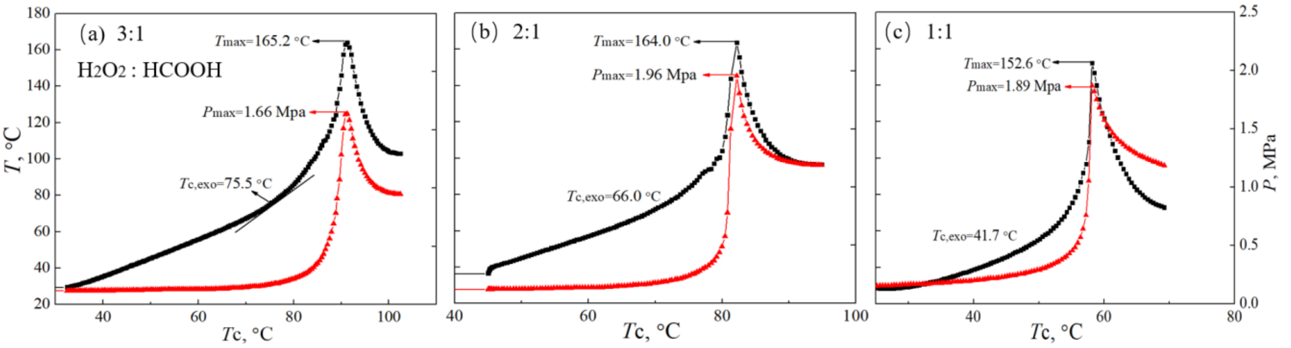


**Fig. 5.** Temperature and pressure evolutions of the mixture of $H_2O_2$ with various contents of formic acid in RSD test.

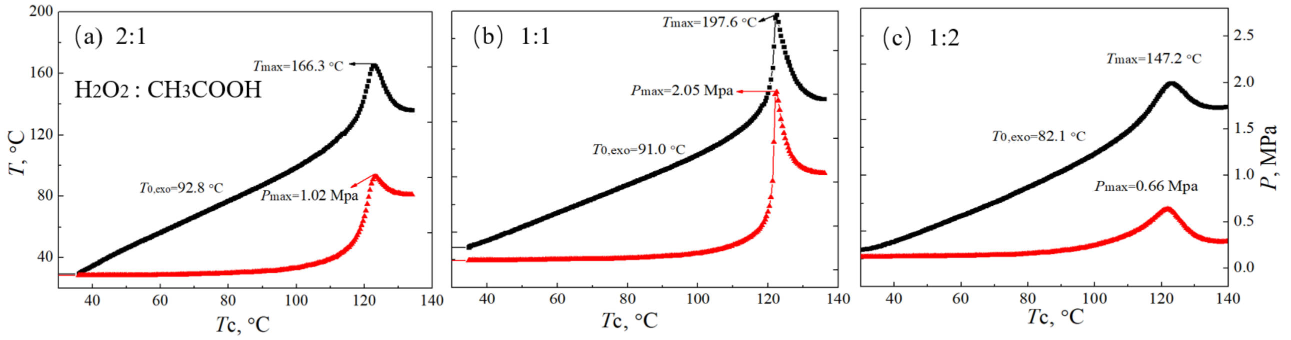


**Fig. 6.** Temperature and pressure evolutions of the mixture of $H_2O_2$ with various contents of acetic acid in RSD test.

Figure 7 shows the effect of HCOOH and $CH_3COOH$ on the thermal runaway of $H_2O_2$ in ARC test. Unlike a regular close system with a constant heating rate in RSD test, the initial exothermic temperature of the mixture of $H_2O_2$ with or without organic acid in an adiabatic system are much lower. The details of the measured parameters in ARC test are summarised in Table 2. Clearly, the presence of HCOOH dramatically accelerates the decomposition of $H_2O_2$, decreasing initial exothermic temperature ($T_{0, exo}$) by 34 °C and final exothermic temperature ($T_{f, exo}$) by 19.3 °C, while the presence of $CH_3COOH$ has a comparatively small effect on this process decreasing $T_{0, exo}$ by only 4.8 °C and $T_{f, exo}$ by 19 °C. As shown in Fig .7b, both the addition of HCOOH and $CH_3COOH$ decrease the maximum pressure ($P_{max}$) since less volume of $H_2O_2$ was used in the mixture than the pure $H_2O_2$ (see Table 2): i.e., 0.98 g for pure $H_2O_2$, while 0.54 g and 0.595 g for $H_2O_2$/HCOOH and $H_2O_2/CH_3COOH$, respectively. The pressure almost shows a linear correlation with temperature, especially when the temperature is no more than 100 °C as shown in Fig. 7c. This is because at low temperatures all the pressure rise in the adiabatic system is contributed by the $O_2$ generation from the $H_2O_2$ decomposition, and the contribution of vapours is ignorable, following the ideal gas law.

Figure 8 compares the correlation of temperature rise rate vs. temperature for the mixture of $H_2O_2$ with and without organic acid in ARC test. It reveals that the addition of HCOOH dramatically increases the maximum temperature rise rate ($r_{max}$) by around 12-fold from 0.75 °C/min to 8.72 °C/min, whilst the addition of $CH_3COOH$ decreases $r_{max}$ to 0.17 °C/min. Globally, the presence of HCOOH significantly increases the thermal runaway risk of $H_2O_2$, while $CH_3COOH$ has a comparatively small effect on $H_2O_2$ at low temperatures. Note that the temperature rise rate has two peaks for the exothermic decomposition of $H_2O_2$ at 83 °C and 102 °C respectively, suggesting that the decomposition can be divided into two parts. Moreover, no explosion was detected for the mixture of $H_2O_2$/HCOOH and $H_2O_2/CH_3COOH$ in this work, but our previous work (Wu et al. 2018) found that the mixture of $H_2O_2$/HCOOH or $H_2O_2/CH_3COOH$ had an explosion in a closed vessel heated to a certain temperature (80 °C for 60 mL $H_2O_2$/60 mL HCOOH and 150 °C for 60 mL $H_2O_2$/ 60 mL $CH_3COOH$). This is probably because the reaction mechanism varies with ambient temperature, and size-effect may also contribute.

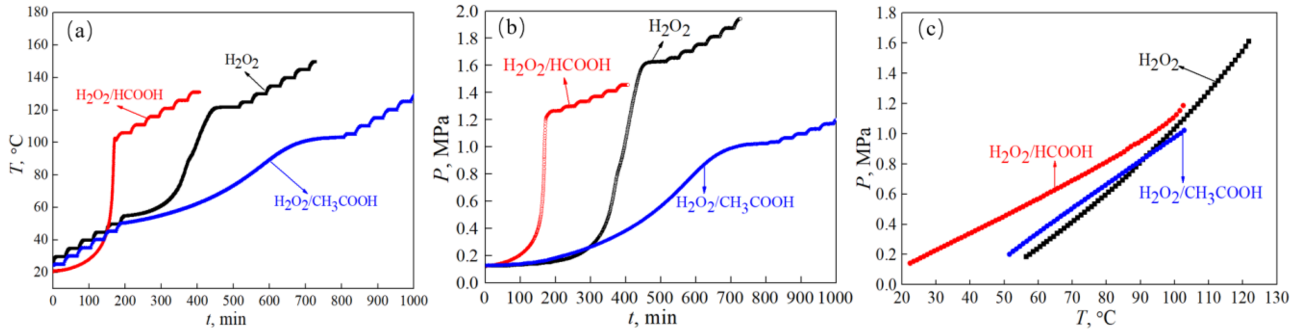


**Fig. 7.** Evolution of the mixture of $H_2O_2$ with and without organic acid in ARC test: (a) temperature, (b) pressure, and (c) pressure vs. temperature.

**Table 2** Measured thermal decomposition characteristic data of samples in ARC test.

| parameters | $H_2O_2$ | $H_2O_2$/HCOOH | $H_2O_2/CH_3COOH$ |
|---|---|---|---|
| mass ($m$), g | 0.98 | 1.08 | 1.19 |
| specific heat ($c_v$), kJ/kg-K | 3.72 | 3.03 | 2.98 |
| initial exothermic temperature ($T_{0,exo}$), °C | 56.4 | 22.4 | 51.6 |
| initial temperature rise rate ($r_0$), °C/min | 0.037 | 0.043 | 0.039 |
| final exothermic temperature ($T_{f,exo}$), °C | 121.8 | 102.5 | 102.8 |
| adiabatic temperature rise ($\Delta T_{ad}$), °C | 65.4 | 80.1 | 51.2 |
| temperature at maximum temperature rise rate ($T_{max}$), °C | 83.6 | 89.3 | 86.7 |
| time to maximum temperature rise rate ($t_{max}$), min | 123.55 | 122.97 | 354.75 |
| maximum temperature rise rate ($r_{max}$), °C/min | 0.75 | 8.72 | 0.17 |
| maximum pressure ($P_{max}$), MPa | 1.61 | 1.19 | 1.02 |
| maximum pressure per mass ($P_{max}/m$), MPa/g | 1.64 | 0.95 | 0.86 |
| total heat of reaction ($Q$), J | 727.08 | 903.99 | 568.04 |
| specific reaction heat ($q$), J/g | 740.49 | 721.64 | 477.22 |

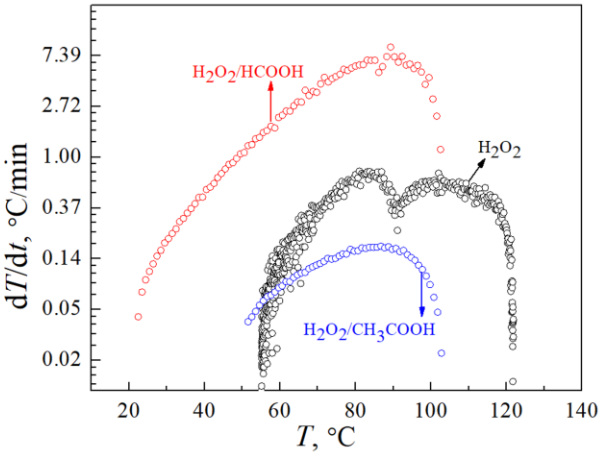


**Fig. 8.** The correlation of temperature rise rate vs. temperature for the mixture of $H_2O_2$ with and without organic acid in ARC test.

## 4. Assessment of kinetic parameters

For a one-step reaction, the self-heat rate at an arbitrary temperature $T$ in an adiabatic system can be expressed as (Townsend et al., 1980)

$$r_{\mathrm{T}} = k\Delta T_{\mathrm{ad}}\left(\frac{T_{\mathrm{f,\,exo}}-T}{\Delta T_{\mathrm{ad}}}\right)^{n} \tag{1}$$

where $\Delta T_{\mathrm{ad}}$ is the adiabatic temperature rise ($\Delta T_{\mathrm{ad}}=T_{\mathrm{f,\,exo}}-T_{\mathrm{0,\,exo}}$), $n$ is the order of the reaction, $T_{\mathrm{f,\,exo}}$ is the final exothermic temperature, $k$ is the rate constant which can be expressed by Arrhenius law as

$$k = A\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \tag{2}$$

where $R$ is the molar gas constant ($R$=8.314J/mol-K), $A$ and $E_{\mathrm{a}}$ are the pre-exponential factor and the apparent activation energy, respectively. Combining with Eq. (1) and rearranging Eq. (2), we have

$$\ln k = \ln\left(\frac{r_{\mathrm{T}}}{\left(\frac{T_{\mathrm{f,\,exo}}-T}{\Delta T_{\mathrm{ad}}}\right)^{n}\Delta T_{\mathrm{ad}}}\right) = \ln A - \frac{E_{\mathrm{a}}}{RT} \tag{3}$$

where the left-hand side can be obtained from ARC test, and it has a linear correlation with 1/$T$. Therefore, $A$ and $E_{\mathrm{a}}$ can be derived from the intercept and the slope of the linear fitting. Although it is well known that $H_2O_2$ decomposition reaction is a typical first order reaction (Lu et al., 2006; Liu et al., 2010), the reaction order for the mixture of $H_2O_2$ with organic acid has not been well studied. Therefore, the order of the reaction is determined first.

Considering the exothermic decomposition of $H_2O_2$ has two parts mentioned above, the kinetic parameters of $H_2O_2$ decomposition should be calculated in two temperature ranges to get the linear correlation according to Eq. (3). 90 °C is selected as the critical value (see Fig. 8). Then ln$k$–1000/$T$ linear fittings with various reaction orders for pure $H_2O_2$, the mixture of $H_2O_2$/HCOOH and $H_2O_2/CH_3COOH$ can be obtained illustrated in Fig. 9. The results show that $H_2O_2$ decomposition is confirmed as a first order reaction in the whole reaction process, and the addition of HCOOH and $CH_3COOH$ acids do not change the reaction order. Note that there are several scatter-points away from the linear fitting at the high temperature region for all the cases in Fig. 9. This means that the reaction mechanism might change, and the reaction tends to be more complicated at high temperatures. And the intermediates are still unclear, thus the further investigation on the reaction mechanisms and details of reaction pathways is required in future works.

The kinetic parameters of the one-step thermal runaway reaction of 30% $H_2O_2$ with or without organic acid are listed in Table 3. The activation energy of the mixture of $H_2O_2$/HCOOH and $H_2O_2/CH_3COOH$ is lower than that of pure $H_2O_2$, so the organic acid has advanced the thermal decomposition of hydrogen peroxide. The kinetic parameters of the 30% $H_2O_2$ decomposition obtained in this work are comparable with the result evaluated by (Liu et al., 2010). The deviation of the apparent activation energy and the pre-exponential factor is probably caused by the different linear fitting subsections, i.e., 90 °C was taken in this work, while 75 °C was selected in Liu et al. (2010). Compared to $H_2O_2/CH_3COOH$, the mixture of $H_2O_2$/HCOOH has a much higher pre-exponential factor which compensates the effect caused by the higher apparent activation energy. Consequently, the mixture of $H_2O_2$/HCOOH has a higher thermal runaway risk than the $H_2O_2/CH_3COOH$ mixture observed by RSD and ARC tests.

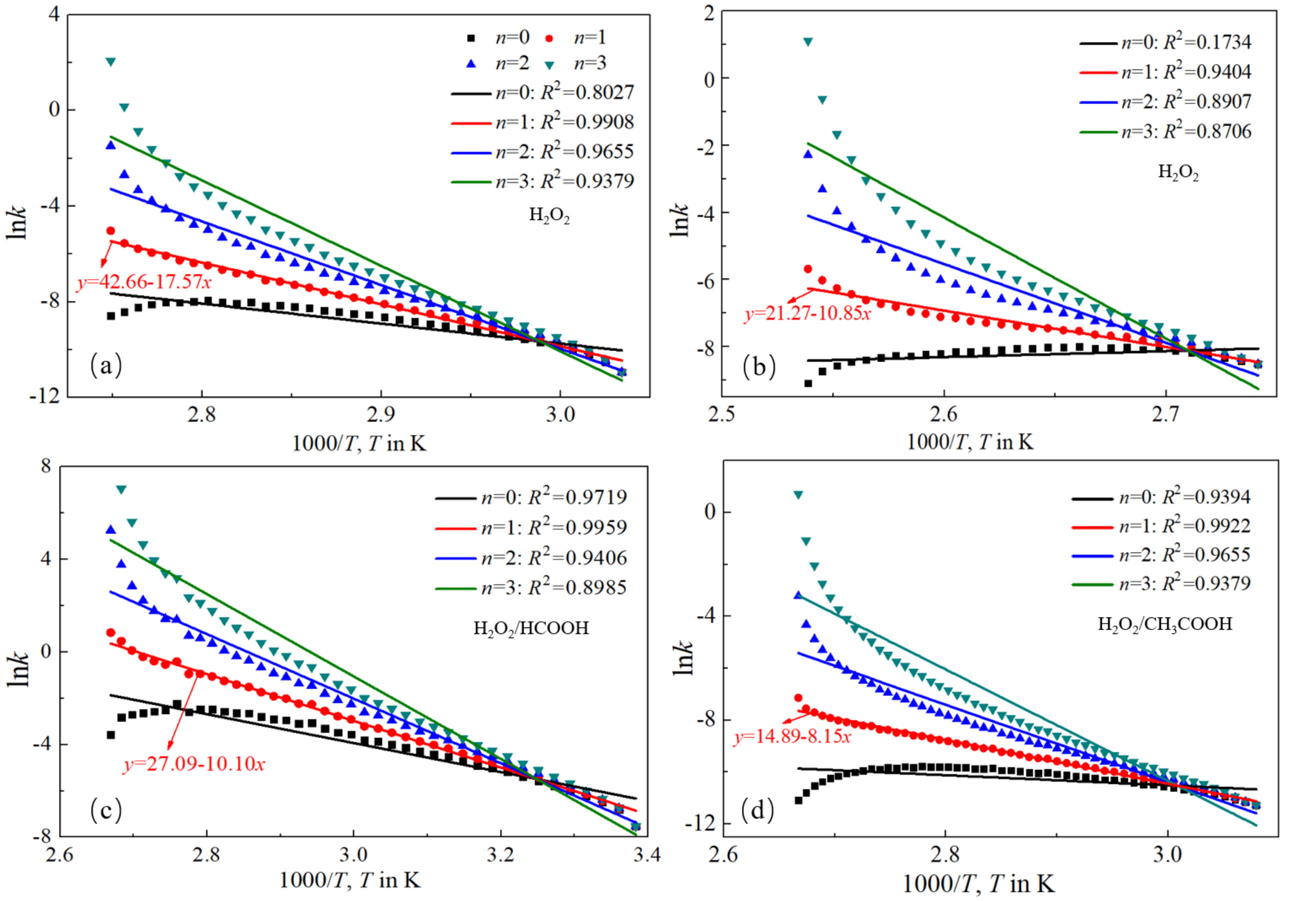


**Fig. 9.** ln*k*−1000/*T* linear fittings with various reaction order: (a) $H_2O_2$ (<90 °C), (b) $H_2O_2$ (>90 °C), (c) $H_2O_2$/HCOOH and (d) $H_2O_2/CH_3COOH$.

**Table 3** Kinetic parameters of tested samples.

| kinetic parameter | $H_2O_2$ | | $H_2O_2$ (Liu et al., 2010) | | $H_2O_2$/HCOOH | $H_2O_2/CH_3COOH$ |
|---|---|---|---|---|---|---|
| | <90 °C | >90 °C | <75 °C | >75 °C | | |
| $n$ | 1 | 1 | 1 | 1 | 1 | 1 |
| $A$, 1/s | 3.37e18 | 1.73e9 | 2.6e23 | 7.2e6 | 5.82e11 | 9.58e5 |
| $E_a$, kJ/mol | 145.55 | 90.18 | 161.48 | 83.60 | 83.97 | 70.24 |

## 5. Conclusions

In this work, a series of experiments were firstly conducted to analyse the thermal hazard of hydrogen peroxide with both inorganic salts or organic acids, and then a one-step global reaction kinetic model characterized as adiabatic temperature increase and final exothermic temperature was briefly described to estimate the kinetic parameters of the mixture of $H_2O_2$ with/without organic acid. Results showed that both the metal ions and their corresponding inorganic acid ions have significant impacts on the thermal runaway of $H_2O_2$: the catalytic effect of metal ion follows $Fe^{2+} > Fe^{3+} > Cu^{2+}$, and the synergistic effect of inorganic acid ion follows $Cl^- > SO_4^{2-}$. In addition, the analysis showed that the runaway reaction of $H_2O_2$ with formic acid or acetic acid is a first order reaction at a low temperature range (< 100 °C) and the thermal runaway risk followed $H_2O_2$/HCOOH > $H_2O_2/CH_3COOH$. Unlike the batch reactor tests in our previous work (Wu et al., 2018), no explosion was found for the mixture of $H_2O_2$/organic acids in this work because of the small sample mass or the reactions at low-temperature region, suggesting a strong size effect and an environmental temperature effect. These results improve our understanding of the thermal runaway behaviour of $H_2O_2$ with incompatible substances at low temperatures.

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