

1 The influence of ClO^- and acidity in the reaction between H_2O_2 and CuCl_2
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11

12 Abstract

13 The potentially explosive reaction of hydrogen peroxide (H_2O_2) and copper chloride (CuCl_2)
14 was investigated. Pressure tests revealed that the reaction was strongly temperature - dependent
15 and can easily undergo runaway reaction. Nevertheless, there was only a slight pressure
16 increase at the low temperatures studied or when using low concentrations of CuCl_2 . Under the
17 conditions generating the slight pressure increase, hypochlorite anions (ClO^-) are generated
18 and the acidity increases. As the reaction reaches completion, ClO^- disappears, and the acidity
19 decreases. Interestingly, the addition of phosphate buffer to maintain the weakly acid
20 conditions led to a runaway reaction, and the use of basic ClO^- promoted the exothermic
21 reaction. Based on the results, acidity has a strong impact on the reaction behaviour.

22

23 Keywords: Hydrogen peroxide, copper chloride, runaway reaction, phosphate buffer, induction
24 period

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1

2 1. Introduction

3 Hydrogen peroxide (H_2O_2) has been widely-used since it was first commercially
4 manufactured in 1818 (Craig and Clark, 1999). Because its decomposition results in the release
5 of very active oxidants such as $\cdot\text{OH}$, its applications range from oxidation in fine chemical
6 synthesis, polymerisation initiation (Gawdzik, et al., 2003), and bleaching (Zeronian and
7 Inglesby, 1995; Naik, et al., 2006). The products of the decomposition of H_2O_2 are harmless O_2
8 and H_2O , and this minimal waste means that H_2O_2 can be used for environmental and
9 biological purposes, for example, wastewater treatment (Li, et al., 2020) and sterilisation in the
10 food industry (Scaramuzza, et al., 2020).

11 Industrially, a large amount of H_2O_2 is used, so, safe handling is crucial, especially because of
12 its reactivity. Despite its long history of commercial and industrial use, accidents involving
13 H_2O_2 still occur. For example, in Japan, an explosion occurred at an impurity removal tank in a
14 H_2O_2 production plant at Ibaraki in 2015. Fortunately, the fire left no injuries and was
15 extinguished in 2 h (Asahi Shinbun, 2015). In 2012, the synthesis of a herbicide using H_2O_2
16 led to an explosion that blew off the roof and the walls of the plant (Asahi Shinbun, 2012).
17 Thus, the safety issues regarding the use of H_2O_2 are still important.

18 As shown by these examples, H_2O_2 can undergo violent reactions, particularly in the
19 presence of impurities such as iron, and there have been some reports concerning the runaway
20 reaction hazard of H_2O_2 caused by contamination (Shu and Yang, 2002). In a previous study,
21 the report of an explosion in a tank car raised awareness of the induction period before a
22 vigorous reaction between H_2O_2 and CuCl_2 (Kumasaki, 2006). In this accident, an unused
23 H_2O_2 and CuCl_2 aqueous solution violently exploded a few hours after mixing, even though
24 H_2O_2 did not seem to react with the CuCl_2 solution initially while the violent reaction with
25 FeCl_3 was observed. In that study, the reaction of H_2O_2 and CuCl_2 was studied to identify the
26 conditions required to induce the induction period. It was found the concentration dependence
27 of CuCl_2 , and that the chloride anion (Cl^-) plays the key role because nitrate (NO_3^-) and
28 sulphate (SO_4^{2-}) only result in mild heat generation in the presence of H_2O_2 under the same
29 conditions. The reaction between CuCl_2 and H_2O_2 showed a characteristic feature: the
30 generation of dark brown suspended particles during the reaction that disappeared after the
31 reaction. Finally, a blue transparent solution was obtained, the colour of which originates from
32 Cu^{2+} .

33 Eto et al. conducted runaway reaction tests of H_2O_2 and CuCl_2 in open cylindrical glass
34 vessels with volumes of approximately 80 (Eto et al., 2009) and 100 mL (Eto et al., 2006) and
35 recorded the temperatures during the reaction. For the reactions in the 100 mL vessel, the time
36 required to reach the maximum temperature and temperature profiles showed a strong
37 dependence on the ambient temperatures and Cu^{2+} concentrations. For the reaction in the 80
38 mL vessel, they demonstrated the positive effect of chloride ions, which promoted the runaway
39 reaction, in contrast to nitrate (NO_3^-) and sulphate (SO_4^{2-}) ions, as in the previous study
40 (Kumasaki, 2006). However, the reaction as a function of Cl^- nor the mechanism of the
41 reaction has been revealed yet.

1 To expand fundamental knowledge and clarify the reaction mechanism to ensure safe
2 handling, in the present study, the reaction between H_2O_2 , Cu^{2+} , and Cl^- was investigated. We
3 observed trends in pressure generation, which are crucial for understanding the risk of
4 container burst, and enabled us to set the conditions of subsequent experiments. Then the ions
5 produced from Cl^- during the reaction was analysed. The ability to promote the reaction was
6 tested using additives, such as chloride and its oxide anions using a reaction calorimeter. In
7 addition, the effect of the pH of the reaction mixture was also analysed.

8 9 2. Experiments

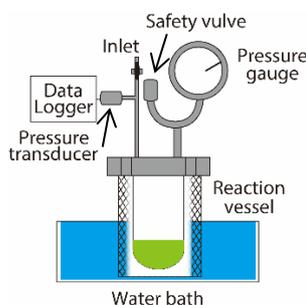
10 2.1 Chemicals and sample preparation

11 The main substances used in the experiments were stabilizer-free H_2O_2 (30 wt%) and copper
12 chloride (II). The CuCl_2 solution was prepared in deionised distilled water by dissolving the
13 solid to obtain a 1 mmol/g solution. Other chemicals are described in the following sections.

14 All chemicals used in the experiments were purchased from Fujifilm Wako Pure Chemical
15 Corporation.

16 17 2.2 Pressure tests

18 The reactions with H_2O_2 were conducted in a small pressure reactor (Tynclave Glass, Büchi AG).
19 The internal reactor volume was 10 mL. A schematic drawing of the experiments is shown in
20 Figure 1. The changes in pressure were detected and recorded with a pressure transducer
21 (PX-409-5.0KGV, Omega Engineering Inc.) and a data logger (midi Logger GL240-UM-801,
22 Graphitec Corporation). The temperature was controlled using a circulator (F25-MV, Julabo
23 GmbH). The reaction vessel is surrounded by a protective mesh which held the vessel.



24
25 Figure 1. Schematic diagram of the pressure test experimental setup

26
27 Before the reaction, 0.5 mL of H_2O_2 and the additive (if any) were introduced into the reactor
28 and maintained at each reaction temperature. The copper solution was injected through a
29 polytetrafluoroethylene (PTFE) tube with a syringe to avoid contamination and ensure accurate
30 and complete addition, as described in a previous study (Kumasakai et al., 2003). The valve
31 was closed after the injection and the pressure profile was recorded.

32 33 2.3 Ion chromatography for Cl^- and its oxidation products

34 Ion chromatography was conducted for the reaction mixture of H_2O_2 and CuCl_2 to identify
35 products derived from Cl^- . The analytes representing the mixture after completion of the

1 reaction were prepared by adding 0.05 g of the CuCl_2 aqueous solution to 0.5 mL of H_2O_2 . To
2 observe the ions formed during the reaction, mixtures of 0.02 g of the CuCl_2 aqueous solutions
3 and 0.5 mL of H_2O_2 were prepared. The mixed solutions were sampled at approximately 1/6, 2,
4 24, and 48 h after mixing. After one-thousand-fold dilution, the analytes were injected through
5 a 13-mm Acrodisc syringe filter with 0.2- μm GHP membrane (Pall Corporation) into a vial in
6 the autosampler. For the identification of ions, standard solutions of Cl^- , ClO_2^- , and ClO_3^- were
7 used. Their concentrations were 5, 10, and 10 ppm, respectively. ClO_4^- is relatively
8 hydrophobic and, thus, appears after the other ions (Showa Denko, 2020). A suppressor-type
9 chromatograph (HIC-20ASP (Shimadzu)) was used with an analytical column (Shodex IC
10 SI-52 4E). The sample injection volume in all cases was 50 μL . The eluent was 3.6 mM of
11 Na_2CO_3 at a flow rate of 0.8 mL/min at 9.0 MPa.

12 13 2.4 UV-Vis spectroscopy for ClO^- detection

14 The detection of hypochlorite ion (ClO^-) was achieved using *N,N*-diethyl-*p*-phenylene
15 diamine (DPD) (FUJIFILM Wako Pure Chemical Corporation, 2020). In the procedure, 0.5 g
16 of DPD reagent was dissolved in 2.5 mL of phosphate buffer (pH 6.5). Both reagents were of
17 sufficient grade for residual chlorine analysis.

18 The analytes representing the mixture after completion of the reaction were prepared by
19 adding 0.2 g of the CuCl_2 aqueous solution to 2 mL of H_2O_2 . To observe the ions formed
20 during the reaction, mixtures of 0.04 g of the CuCl_2 aqueous solutions and 2 mL of H_2O_2 were
21 prepared. The mixed solutions were sampled at approximately 2, 24, and 48 h after mixing. As
22 references, 0.2 g and 0.04 g of the CuCl_2 aqueous solutions were used.

23 The analyte was diluted 100 times, and the diluted reaction mixture was added to the
24 DPD/phosphate buffer solution to make the solution up to 50 mL in a volumetric flask.

25 A sample solution in a quartz cuvette was measured using a UV-Vis spectrometer (V-560,
26 JASCO Corporation) between 190 and 900 nm with a resolution of 0.5nm. The scan speed was
27 200 nm/min. The typical absorption bands of oxidised DPD appear at 510 and 555 nm (Akai,
28 et al., 2009).

29 30 2.5 pH measurements

31 The pH of the H_2O_2 solution was measured before, during, and after the reaction with CuCl_2 ,
32 using a pH meter (LAQUA twin pH-11B, Horiba, Ltd.). To determine the pH of the reaction
33 mixture, 2 mL of H_2O_2 was placed in a vial and 0.04 g of the CuCl_2 solution was added. The
34 pH was monitored at 1/12, 12, 24, and 48 hours. To achieve a vigorous runaway reaction, 0.2g
35 of the CuCl_2 solution was mixed with H_2O_2 , and pH was measured after the reaction had
36 completed. As a reference, 0.2 g and 0.04 g of the CuCl_2 solution were diluted in 2 mL of
37 water to obtain 0.1 mol/L and 0.02 mol/L aqueous solutions.

38 39 2.6 Reaction calorimetry

40 The understanding of the dynamic effect of the additives is required to ensure safe handling.
41 For this purpose, a reaction calorimeter was employed, and this enabled us to add additives by

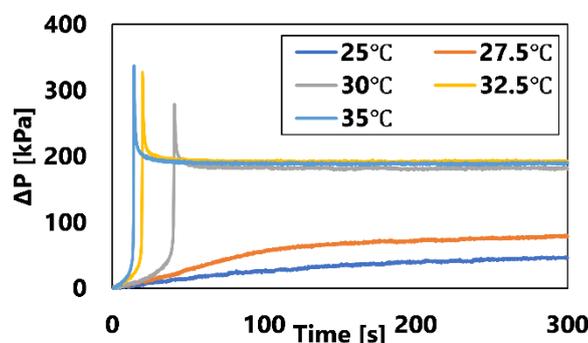
1 injection after the start of reaction between H_2O_2 and CuCl_2 .

2 The calorimetry measurements were used to observe the changes in reaction behaviour after
3 the injection of additives. A schematic view of the reaction calorimeter has been provided in
4 our previous work (Nishiwaki, 2019). The calorimeter allows us to measure the heat flow
5 triggered by the addition of substances because it is a semi-closed system.

6 In the measurements, 0.5 mL of H_2O_2 in a vial was placed in the calorimeter. After the heat
7 flow was stabilised at 30 °C, 0.02g of the CuCl_2 solution was injected through a PTFE tube to
8 trigger the reaction. Five minutes later, 0.05 g of the additive solution (NaClO , NaCl , or HCl)
9 was injected through the PTFE tube. The additive solutions were prepared at a concentration of
10 1 mmol/g. In the control experiments, the same amount of water was injected to compensate
11 for the effect of dilution by solvent water.

13 3. Results and Discussion

14 3.1 Pressure test



16
17 Figure 2 Pressure profiles of H_2O_2 with 0.05 g of CuCl_2 solution.

18
19 Figure 2 shows the pressure profiles recorded at different initial temperatures using 0.05 g of
20 the CuCl_2 aqueous solution. The profiles showing a steep pressure increase indicate a runaway
21 reaction. Of the conditions leading to runaway reactions, after the H_2O_2 and CuCl_2 aqueous
22 solutions were mixed, the use of higher temperatures resulted in the maximum pressure
23 occurring sooner. However, the reaction at lower temperatures showed a significant difference
24 from those at higher temperatures. The low-temperature profiles show a slight increase in
25 pressure but without a spike over the course of the experiment.

26 In the case of the experiments with 0.075 g of CuCl_2 solution, the reaction mixture underwent
27 a runaway reaction at 22.5 °C (Figure 3) whereas the reaction rate was almost maintained at
28 27.5 °C with 0.05 g of CuCl_2 solution. Figure 4 shows that H_2O_2 with 0.1 g of CuCl_2 solution
29 undergoes a runaway reaction at 20 °C, whereas the reaction with 0.075 g of CuCl_2 solution did
30 not undergo runaway. Thus, the conditions leading to the suppressed reaction have been
31 identified for use in subsequent experiments.

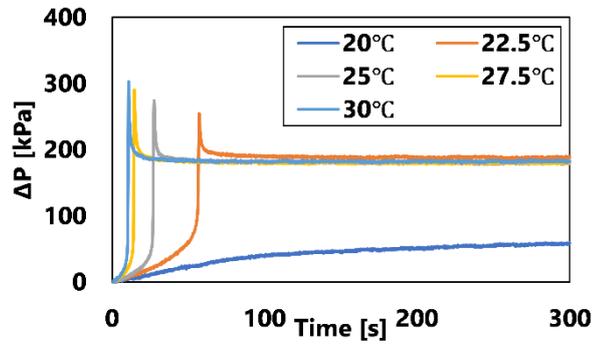


Figure 3 Pressure profiles of H₂O₂ with 0.075 g of CuCl₂ solution.

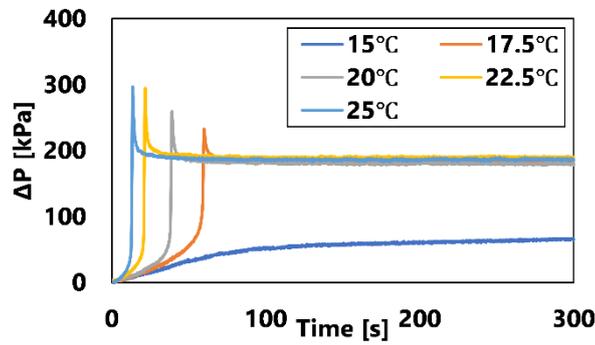


Figure 4 Pressure profiles of H₂O₂ with 0.1 g of CuCl₂ solution.

3.2 Ion chromatography

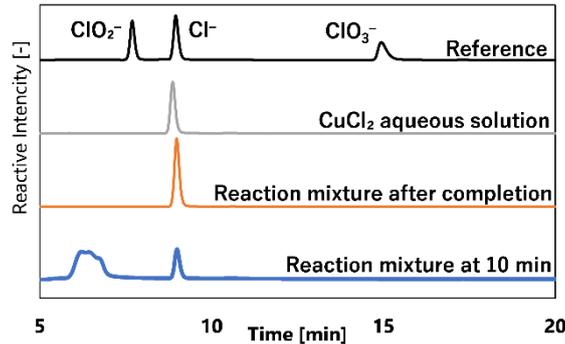


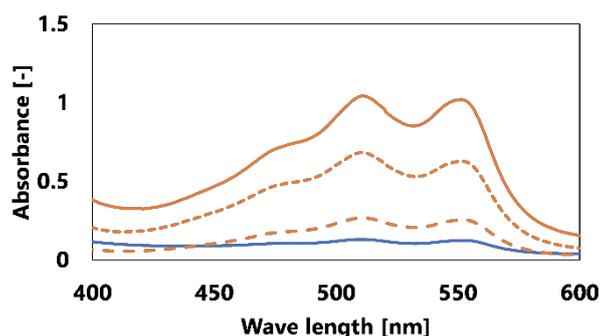
Figure 5 Ion chromatograms.

Figure 5 shows the result of ion chromatography for the identification of solution state anions formed from Cl⁻. Neither chlorite nor chlorate were found in the mixtures, but chloride ions were found during and after the reaction and, obviously, in the CuCl₂ solution. Because no clear peak was detected after the given retention time at which ClO₃⁻ should appear, we concluded that ClO₄⁻ was not present. Interestingly, a broad peak emerged at around 6 min in

1 the mixture sampled during the reaction, but disappeared in the mixture after the reaction.

2

3 3.3 UV-Vis spectroscopy for ClO^- detection



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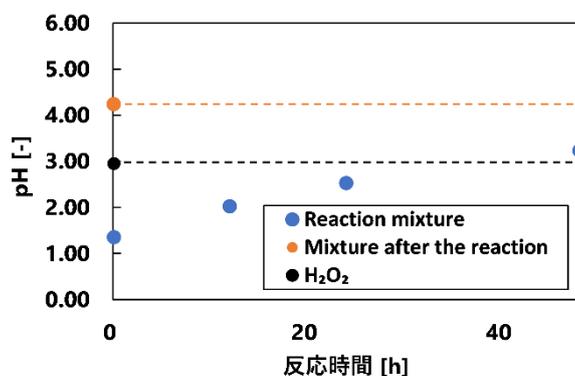
5 Figure 6 UV-Vis spectra using DPD analysis for reaction mixtures. Upper solid line is
6 reaction mixture at 2h, short dashed line is reaction mixture at 24 h, long dashed line is
7 reaction mixture at 48 h, lower solid line is reaction mixture after completion.

8

9 Another possible ion that can be derived from Cl^- is ClO^- , so DPD analysis was conducted
10 for the reaction mixtures. Figure 6 shows the significant absorption bands of the semi-quinoid
11 cationic Würster dye (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) formed during the reaction.
12 The absorption was attributed to the oxidation of DPD by HClO/ClO^- (Harp, 2002), so we
13 conclude that oxidising hypochlorite ions are generated during the reaction but disappear by
14 the end of the reaction.

15

16 3.4 pH measurements



17

18 Figure 7 pH changes during the reaction.

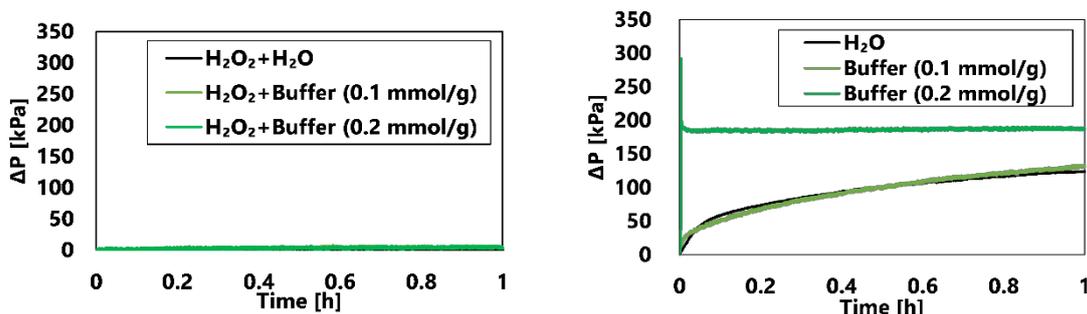
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20 Figure 7 shows pH behaviour as a function of time. Before mixing, the pH of H_2O_2 , 0.1
21 mol/L of CuCl_2 aqueous solution, and 0.02 mol/L of CuCl_2 aqueous solutions were 2.95, 4.25,
22 and 4.67, respectively. The H_2O_2 and CuCl_2 aqueous solutions are weakly acidic. With the
23 addition of CuCl_2 solutions, the acidity of the H_2O_2 solution increased immediately after the
24 mixing and then decreased. With regard to the appearance of the reaction mixtures over the
25 course of the reaction, the reaction mixture was a dark-blown suspension at the early stage of
26 the reaction, becoming transparent blue solution as time progressed. Combining the pH profile

1 and the change in appearance, we conclude that the acidic conditions promote the generation of
2 a suspension, which can impede the runaway reaction.

3

4 3.5 Pressure profile of reaction in the presence with phosphate buffer



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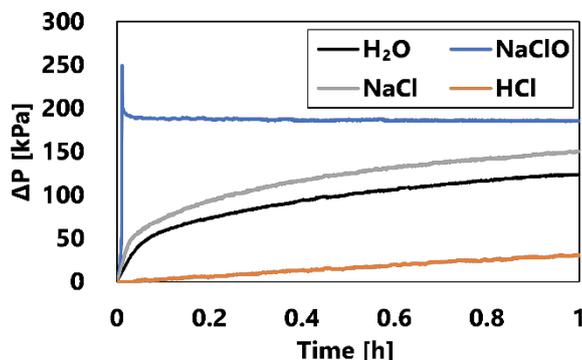
6 Figure 8 Pressure profiles on mixing of H₂O₂ and phosphate buffer (left), and pressure
7 profiles triggered by CuCl₂ in the presence of phosphate buffer (right).

8

9 Based on the pH measurements, the use of phosphate buffer should stabilise the pH. Before
10 investigating the effect of the phosphate buffer on this reaction, we checked that there was no
11 noticeable pressure increase (i.e., reaction) on the mixing of H₂O₂ and the buffer alone (Figure
12 8 (left)). Figure 8 (right) shows the pressure profiles of the reaction (0.5 mL of H₂O₂ and 0.05 g
13 of CuCl₂) in the presence of 0.05 g of phosphate buffer. On mixing H₂O₂ with 0.1 mmol/g of
14 phosphate buffer (5.0×10^{-6} mol of phosphate), a pressure profile similar to that of the control
15 experiment in which an equivalent amount of water was added to H₂O₂ was obtained. However,
16 with 0.2 mmol/g of phosphate buffer (1.0×10^{-5} mol of phosphate), a runaway reaction
17 occurred. In contrast, as shown in the previous section, the combination of 0.5 mL of H₂O₂ and
18 0.05 g of the CuCl₂ aqueous solution resulted in the suppression of a runaway reaction at 25 °C.
19 (Fig.2). Thus, the reaction containing a sufficient amount of phosphate buffer was vigorous,
20 even under the condition that we have previously shown to induce an induction period.

21

22 3.6 Reaction of H₂O₂ in the presence of different Cl sources: HCl, NaCl, and NaClO



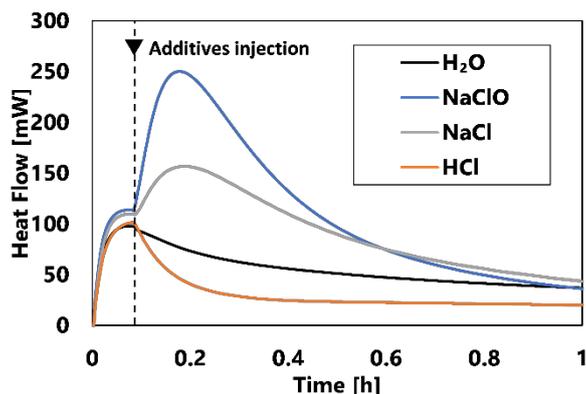
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24 Figure 9 Pressure profiles on mixing H₂O₂ with Cl⁻ or ClO⁻.

25

26 The pressure profiles of the reaction in the presence of an acid source of Cl⁻, a neutral source

1 of Cl^- , and a basic source of ClO^- are shown in Figure 9. The addition of HCl suppressed the
 2 pressure increase, whereas the reaction with neutral NaCl promoted heat generation more than
 3 the reaction with the same amount of water, which is shown for comparison. On contrast, the
 4 addition of NaClO resulted in a runaway reaction.



5
 6 Figure 10 Calorimetry of the H_2O_2 and CuCl_2 reaction and changes after the addition of
 7 additives.

8
 9 Table 1 Summary of the heat generation

Additives	Heat generation [kJ/g]
H_2O	3.55
NaClO	3.60
NaCl	3.60
HCl	2.73

10
 11
 12 The dynamic change in the heat flow with the addition of Cl^- or ClO^- is shown in Figure 10.
 13 The heat flow profiles show the same trend for each Cl source as the pressure profiles: NaClO
 14 and NaCl promoted the exothermic, pressure-increasing reaction, whereas HCl restrained it.
 15 Table 1 indicated that the heat generation little changed by additives except HCl.
 16 Although ClO^- ions were observed under the condition of suppressing a runaway reaction, the
 17 reaction mixture with NaClO deliberately added in the calorimetry experiments behaved
 18 differently and showed a positive impact on the generation of a runaway reaction.

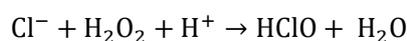
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 20 4. Discussion

21 In this study, we have focused on the behaviour of Cl^- and the influence of acidity in the
 22 reaction of H_2O_2 and CuCl_2 , particularly during slow reactions.

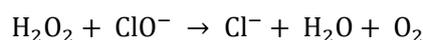
23 The pressure tests revealed the remarkable temperature dependence of this reaction. Some
 24 studies of the reaction between H_2O_2 and CuCl_2 have been carried out, but they mainly aimed
 25 at simulating the reaction in seawater (Moffett and Zika, 1987) and organisms (Rothschild and
 26 Tuft, 1950), and involved the use of low-concentration and low-volume analytes. Because of
 27 this study focuses on industrial safety and the prevention of runaway reactions, a relatively
 28 large amount and high concentration of analyte were used, revealing the clear differences

1 between the runaway and the suppressed reactions. Based on the pressure profiles of the
2 reaction at various initial temperatures, this reaction is highly temperature – dependent. The
3 pressure vessel tests determined the conditions yielding the suppressed reaction for the
4 subsequent investigation in this study.

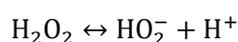
5 Ion chromatography confirmed the presence of Cl^- in all stages of the reaction and the
6 absence of ClO_x^- ($x = 2, 3, \text{ and } 4$). However, unidentified peaks were observed with short
7 retention times (approximately 6 min) and the subsequent DPD analysis demonstrated the
8 presence of ClO^- . Some previous studies have explored the generation of ClO^- , which occurs
9 in the presence of myeloperoxidase as a catalyst for the reaction between Cl^- and H_2O_2 .
10 Harrison and Shultz demonstrated that little ClO^- was generated without the enzyme or H_2O_2
11 under their reaction conditions (Harrison and Schultz, 1976). Frenkel et al. identified the
12 production of ClO^- in solutions of H_2O_2 and Cu^{2+} in the presence of 0.5 M NaCl (Frenkel, et al.,
13 19876) during their research on sea urchins. These studies suggest that some catalysts are
14 required for ClO^- formed from Cl^- and H_2O_2 (KEGG Database)



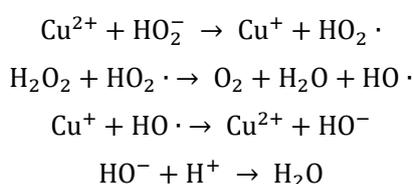
16
17 In contrast, ClO^- is consumed in an aqueous reaction generating singlet oxygen (Khan and
18 Kasha, 1970; Shams El Din, Mohammed, 1998).



19
20
21
22 The peak that appeared in the chromatogram at 6 min has not been identified, and the DPD
23 analysis does not guarantee that the broad peak originated from ClO^- . And unidentified species
24 may exist during the reaction. However, the behaviour of ClO^- suggested that the formation
25 and consumption of ClO^- may contribute the suppression of a runaway reaction. In addition,
26 the experiments also clarified the influence of acidity. H_2O_2 originally dissociates as shown
27 below, which explains the initial pH of the H_2O_2 solution.



28
29
30 The experimental results showed that the acidity increased and decreased during the reaction.
31 Based on the pH changes during the reaction, the pressure profiles and heat release behaviour were
32 examined in the presence of phosphate buffer to maintain the acidity of the reaction mixture. The
33 presence of phosphate buffer resulted in the mixture undergoing a runaway reaction, even when the
34 suppression occurred without phosphate buffer. And the reaction containing NaClO indicated that
35 the effect of acidity has more impact to promote the runaway reaction than the effect of ClO^- to
36 suppress the reaction. In a previous study, the reaction between H_2O_2 and Cu^{2+} was proposed as
37 follows (Kawamura, 2006).



1

2 These reaction steps do not appear to contribute to the increase in acidity. However, the
3 experimental results showed the significant impact of acidity on the reaction between H₂O₂ and
4 CuCl₂. In addition, other unidentified reaction pathways could exist. The result indicate that a
5 runaway reaction caused by an accidental contamination can deter or prevent by controlling
6 acidity of the mixture.

7

8 Conclusion

9 For the safe handling and to expand fundamental knowledge of H₂O₂, the reaction triggered
10 by CuCl₂ was investigated. At the beginning of this study, pressure profiles of the reaction
11 were obtained by varying the amount of CuCl₂ and the initial temperature. Based on the
12 experiments, experimental conditions to suppress a runaway reaction were established. During
13 the conditions, the pH changed: that is, the acidity increased. Interestingly, the presence of
14 phosphate buffer, which should maintain a stable, acid pH, led to a runaway reaction. Based on
15 the results, acidity has a strong impact on the reaction behaviour, and these results provide a
16 useful measure to suppress the transition to a runaway reaction and safe handling of this
17 mixture. An increase in acidity can prevent the reaction from becoming a runaway reaction in
18 case of accidental mixing of H₂O₂ and CuCl₂. Ion chromatography and DPD analysis revealed
19 that ClO⁻ appeared only during the suppressed reaction, whereas chloride anion were in all
20 stages of the reaction. The presence of NaClO promoted exothermic heat release rather than
21 suppressing it. The difference in the influence of ClO⁻ was considered to be attributed to the
22 basicity of the ClO⁻ solution.

23 This study aims to obtain measures to avoid explosive reactions of hydrogen peroxide, and
24 the effects of Cl⁻ and acidity of the reaction liquid were investigated as a basis for further
25 investigation to clarify the mechanism of this reaction.

26

27 Acknowledgement

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29 University for technical assistance with the experiments.

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31

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