

Study on detoxification property of alkaline-modified MoO_4^{2-} - H_2O_2 decontaminants against PhSMe under subzero environment

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Abstract. The decontaminant activated by MoO_4^{2-} (MoO_4^{2-} - H_2O_2) suitable for subzero environment shows strong oxidizing ability and weak nucleophilicity due to its acid. In this paper, in order to improve nucleophilicity and retain oxidation of MoO_4^{2-} - H_2O_2 as far as possible, NH_3 and NaOH were used as alkaline modifiers, and PhSMe was used as a simulant of HD to study the oxidation rate and products of sulfides by alkaline-modified MoO_4^{2-} - H_2O_2 below zero. Results showed that the reaction rate constants decreased with the increase of pH in both NH_3 and NaOH modified MoO_4^{2-} - H_2O_2 at -20°C , and the relative ratio of sulfone to sulfoxide increased especially at $\text{pH}>9$. The reaction activation energy E_a of PhSMe oxidation in the alkaline-modified MoO_4^{2-} - H_2O_2 decontaminants was lower than that in the MoO_4^{2-} - H_2O_2 decontaminant, which indicated that the sensitivity of the oxidation reaction rate to temperature in MoO_4^{2-} - H_2O_2 was reduced after modification.

1 Introduction

Although most chemical warfare agents (CWAs) stocks have been destroyed, they still appeared in some local wars or terrorist attacks, such as the suspected nerve agent attack events in Syria in 2015 and the death of Kim Jong-nam in 2017 [1]. Decontamination, as a technical process to remove/neutralize contaminants from contaminated objects, plays an extremely important role [2, 3]. CWAs still have a great hazard to personnel under subzero environment, hence it is necessary to destroy the toxic chemicals for the contaminated area where personnel and equipment pass, contaminated personnel and equipment. For this, it is obviously very important to study detoxification property of decontaminants applied under subzero environment.

The main decontaminants against CWAs include hypochlorite, base and peroxide. Hypochlorite cannot be used normally below zero due to its high freezing point. Alkali-alcohol-amine decontaminants which can be used under subzero environment show strong corrosiveness to the environment due to its strong basicity. While peroxide decontaminants have developed rapidly in recent years due to their high reactivity with CWAs and low corrosiveness to metals, rubbers, plastics, etc. The well-known ones are DF-200 [4] and Decon Green [5] developed in the United States. Moreover, the hydrogen peroxide decontaminant with a low freezing point can retain high reactivity under subzero environment through adding additives, activators, etc.

The mechanisms of detoxification against CWAs include oxidation and nucleophilicity. H_2O_2 activated by MoO_4^{2-} (MoO_4^{2-} - H_2O_2) shows strong oxidizing ability

and weak nucleophilicity due to its acid, so it has high speed of oxidation on HD (mustard, bis (2-chloroethyl) sulfide) and limited degradation on GD (Soman, pinacolyl methylphosphonofluoridate), which mainly been decontaminated through nucleophilic reaction. In order to improve nucleophilicity and retain oxidation of MoO_4^{2-} - H_2O_2 as far as possible, NH_3 and NaOH were used as alkaline modifiers in the paper.

Thioanisole (PhSMe), with a similar structure to HD and weaker toxicity, has been usually used as a reaction simulator in the decontamination of HD [6]. In this work, PhSMe was used as the probe molecule to compare the oxidation performance between MoO_4^{2-} - H_2O_2 and MoO_4^{2-} - H_2O_2 modified by NH_3 and NaOH . The reaction rate and detoxification products with pH were detected below zero. Through comparing the differences in rate constants and detoxification products in three decontamination solutions, their detoxification property with PhSMe was discussed.

2 Experimental

2.1 Chemicals

30% (wt%) hydrogen peroxide and 28% (wt%) ammonium was purchased from Beijing Chemical Plant. With an A.R. grade, potassium molybdate and propylene carbonate were from West Asia Chemical Inc (Shandong, China). Sodium sulfite (Na_2SO_3) and sodium hydroxide (NaOH) were from Guangfu Fine Chemical Research Institute (Tianjin, China). 15% (wt %) Na_2SO_3 was used as neutralizing solutions. N-hexane (GC grade) and dichloromethane (DCM, GC grade) were obtained from

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Bafang Agents Inc. (Beijing, China). They were as extractants.

The MoO₄²⁻-H₂O₂ decontaminant used in experiments were mixed by 30% hydrogen peroxide and propylene carbonate at a ratio of 6:4 (V: V), and K₂MoO₄ (1wt%) was added.

2.2 Methods

2.2.1 The modification of MoO₄²⁻-H₂O₂

NaOH-MoO₄²⁻-H₂O₂ and NH₃-MoO₄²⁻-H₂O₂ decontaminants were prepared by adding a certain amount of 10 mol·L⁻¹ NaOH solution and 28% NH₃·H₂O into MoO₄²⁻-H₂O₂ decontaminants, respectively. The pH of decontaminants was adjusted. The pH value was detected by the professional experimental pH tester (HI2221 HANNA).

2.2.2 Droplet detoxification experiments

The experiments were done in 25 mL test tubes. Firstly, 20 μL PhSMe in 25 mL test tubes and pre-prepared decontaminants were put in a low temperature constant temperature stirring reaction bath (DHJF-8002) at a preset temperature for 30 minutes. Secondly, 1 mL decontaminant was added to the test tube. After reacting for a certain time under stirring at 800 r/min (i.e. revolutions/minute), 6 mL 15% Na₂SO₃ and 10 mL extractant were added, and immediately shake for 20 s. After standing for 15 min, the extractant layer solution was taken for residual PhSMe determination.

2.2.3 The detection for PhSMe

With a specific absorption at 254 nm [7], PhSMe can be quantitatively detected by a UV-Visible Spectrophotometer (Evolution 220). There were no components that interfered with the ultraviolet absorption of PhSMe in the extractant layer solution.

2.2.4 Product Analysis

The detoxification products were quantitatively analyzed by a mass spectrometric detector (GC-MS (Agilent HP 5890/HP 5971) equipped with an HP-5 capillary column (30 m×0.32 mm×0.25 μm), employing a temperature program (60-280°C at 15°C·min⁻¹) and He as carrier gas.

3 Results and Discussion

3.1 Optimization for extraction

The extraction using n-hexane or DCM was investigated by comparing the PhSMe extraction ratios after reacting for the zero time. The results were showed in Table 1.

Table 1. PhSMe Extraction ratio from decontaminant solutions (n-hexane or DCM as extractant)

| Decontaminants | N-hexane | | DCM | |
|--|----------------------------|---------|----------------------------|---------|
| | PhSMe Extraction ratio (%) | RSD (%) | PhSMe Extraction ratio (%) | RSD (%) |
| MoO ₄ ²⁻ -H ₂ O ₂ | 86.4 | 0.9 | 83.3 | 1.6 |
| NaOH-MoO ₄ ²⁻ -H ₂ O ₂ | 83.6 | 1.6 | 82.2 | 1.7 |
| NH ₃ -MoO ₄ ²⁻ -H ₂ O ₂ | 83.2 | 2.3 | - | - |

Comparing the extraction ratio with n-hexane and DCM, it was found that they all have good extraction capacity for PhSMe in different decontaminants and it showed a slightly better extraction ratio with n-hexane (above 83%) than that with DCM n-hexane. So n-hexane was selected as extractant in the following experiments.

The actual residual concentration of PhSMe (c_t , mg·mL⁻¹) in reaction time of t (min) could be determined by correction with the extraction ratio in zero reacting time (Y , %) as formula (1), where c_t' was the detected residual concentration of PhSMe, mg·mL⁻¹.

$$c_t = c_t' / Y \quad (1)$$

3.2 Effect of pH on the kinetic constant for oxidation of PhSMe in alkaline-modified MoO₄²⁻-H₂O₂ solutions

3.2.1 Kinetic study of detoxification in decontaminant solution

The oxidative detoxification against HD and PhSMe in H₂O₂ decontaminant was regarded as a quasi-first order reaction [8, 9], and the first order kinetic rate constant (k , min⁻¹) could be calculated through formula (2), where c_0 was initial PhSMe added into decontaminant solutions.

$$c_t = c_0 e^{-kt} \quad (2)$$

Figure 1 was the kinetic plot of PhSMe in MoO₄²⁻-H₂O₂ solution at -20°C. It showed a good linear relationship between $\ln c_t / c_0$ and the reaction time. Hence, the following kinetic rate constant was calculated according to the first-order reaction rate formula (2).

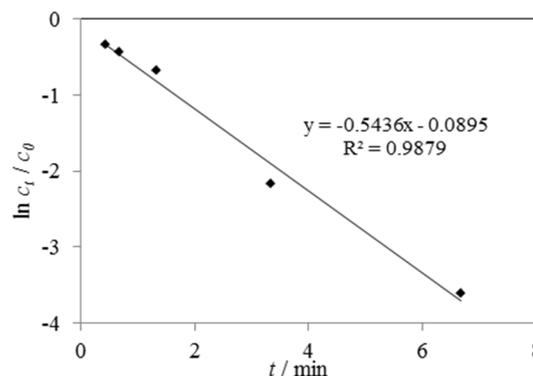


Figure 1. Effect of reaction time on $\ln c_t / c_0$ in MoO₄²⁻-H₂O₂ solution ($T=-20^\circ\text{C}$)

3.2.2 Effect of pH on the kinetic constant for oxidation of PhSMe in alkali modified MoO_4^{2-} - H_2O_2 solution

Figure 2 showed the effect of pH on the kinetic rate constant for oxidation of PhSMe in different decontaminant solutions. The pH ranges of NaOH-MoO_4^{2-} - H_2O_2 and $\text{NH}_3\text{-MoO}_4^{2-}$ - H_2O_2 was 7.0~9.8 and 7.8~9.2 respectively.

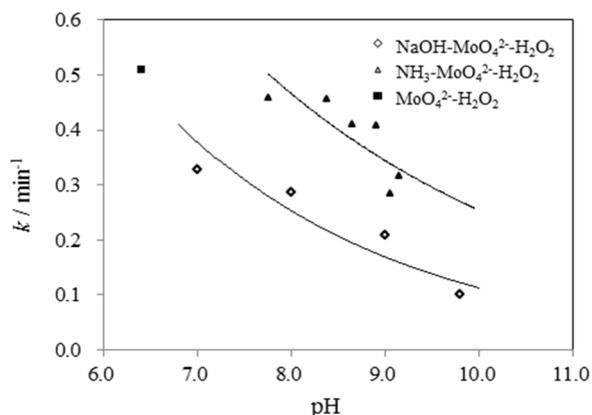


Figure 2. Effect of pH on k for oxidation of PhSMe in alkaline-modified MoO_4^{2-} - H_2O_2 solution ($T=-20^\circ\text{C}$)

At -20°C , the rate constant k of PhSMe oxidation in MoO_4^{2-} - H_2O_2 decontaminant modified by NaOH and NH_3 all decreased with the increase of pH, and the detoxification rate in $\text{NH}_3\text{-MoO}_4^{2-}$ - H_2O_2 decontaminant is higher than that in NaOH-MoO_4^{2-} - H_2O_2 decontaminant.

At the same pH, the difference in the reaction rate constant k of PhSMe in $\text{NH}_3\text{-MoO}_4^{2-}$ - H_2O_2 and NaOH-MoO_4^{2-} - H_2O_2 decontaminants may come from two aspects. On the one hand, under weakly alkaline conditions, the primary oxidation of PhSMe by peroxide was generally considered to be carried out through a solvent-assisted oxygen transfer mechanism [11, 12], and the oxidation reaction rate was linearly related to the $\text{p}K_a$ of the solvent [12]. The $\text{p}K_a$ in $\text{NH}_3\text{-MoO}_4^{2-}$ - H_2O_2 was higher than that in NaOH-MoO_4^{2-} - H_2O_2 , so the reaction rate is correspondingly fast in $\text{NH}_3\text{-MoO}_4^{2-}$ - H_2O_2 . On the other hand, the higher the cation concentration was, the faster the apparent oxidation reaction rate was under the same temperature and pH conditions. The cation (NH_4^+) concentration in $\text{NH}_3\text{-MoO}_4^{2-}$ - H_2O_2 was higher than that (Na^+) in NaOH-MoO_4^{2-} - H_2O_2 , so the reaction rate k was high in $\text{NH}_3\text{-MoO}_4^{2-}$ - H_2O_2 , too.

3.3 Effects of pH on the oxidation products of PhSMe in alkaline-modified MoO_4^{2-} - H_2O_2 solution

The effect of pH on the oxidation products of PhSMe was investigated in alkali-modified MoO_4^{2-} - H_2O_2 solution after the reaction time 30 min at -20°C . The peak area ratio of sulfone to sulfoxide ($A_{\text{sulfone}}/A_{\text{sulfoxide}}$) in different decontaminants with pH was shown in Figure 3.

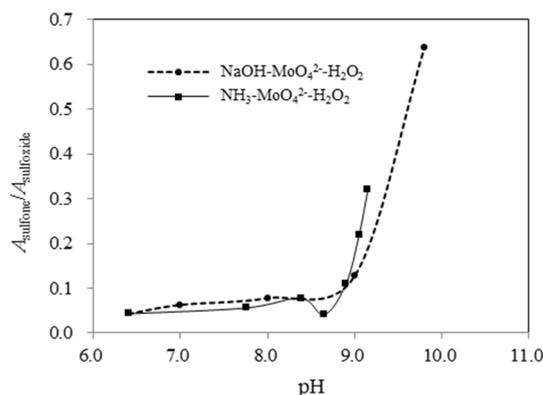


Figure 3. Effects of pH on the oxidation products of PhSMe in alkaline-modified MoO_4^{2-} - H_2O_2 solution ($T=-20^\circ\text{C}$, $t=30$ min)

Figure 3 showed that the relative content of sulfone had an upward trend with the increase of pH. The trend was not significant when the pH was less than 9, and the peak area ratio of sulfone to sulfoxide was less than 0.15 when the pH was about 9. The increase trend was more obvious when pH was more than 9.

Due to the weak alkalinity of NH_3 , the content of highly toxic sulfone as a deep oxidation product could not too high even if it was added excessively in actual use.

3.4 Effect of temperature on the detoxification property against PhSMe in three decontaminants solution

Two alkaline-modified decontaminants with pH close to 9 were chosen to investigate the PhSMe kinetic rate constants of the detoxification within the temperature range (-25°C ~ -10°C), and compared with MoO_4^{2-} - H_2O_2 decontaminant.

Figure 4 showed the good linear relationship between $1/T$ and $\ln k$. The detoxification kinetic constants for oxidation of PhSMe in three decontaminant solutions at different temperatures were shown in Table 3.

The activation energy of the detoxification was calculated according to the Arrhenius equation (3).

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (3)$$

Where, E_a is the reaction activation energy, $\text{J}\cdot\text{mol}^{-1}$; T is the reaction temperature, K; A is the pre-exponential factor, min^{-1} ; R is the ideal gas constant.

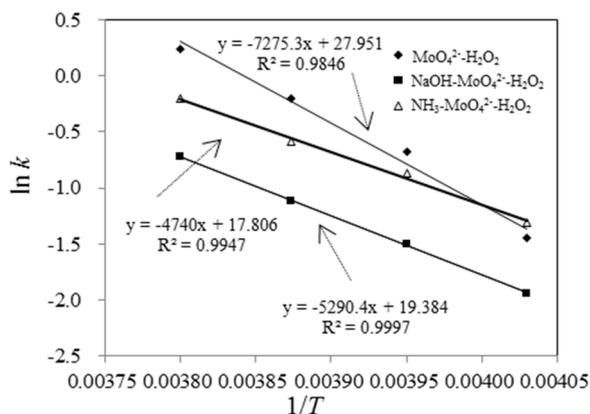


Figure 4. Effect of $1/T$ on $\ln k$ in oxidation of PhSMo in different decontaminants solution (pH \approx 9 in alkaline-modified solution)

Table 2. The detoxification property of three decontaminants against PhSMo under subzero environment

| Decontaminants | pH | Reaction rate constant k / min^{-1} | | | | $E_a / \text{kJ} \cdot \text{mol}^{-1}$ | A / min^{-1} |
|--|-----|--|--------|--------|--------|---|-----------------------|
| | | -10 °C | -15 °C | -20 °C | -25 °C | | |
| MoO ₄ ²⁻ -H ₂ O ₂ | 6.4 | 1.28 | 0.82 | 0.51 | 0.23 | 60.49 | 1.38×10^{12} |
| NaOH-MoO ₄ ²⁻ -H ₂ O ₂ | 9.0 | 0.49 | 0.33 | 0.22 | 0.14 | 44.00 | 2.62×10^8 |
| NH ₃ -MoO ₄ ²⁻ -H ₂ O ₂ | 8.9 | 0.82 | 0.55 | 0.42 | 0.27 | 39.41 | 5.41×10^7 |

It could be seen from table 2 that the apparent oxidation reaction rate constant k in three decontaminants decreased as the temperature decreased. However, the degree of influence was different, which was reflected in the reaction activation energy E_a . E_a of PhSMo oxidation in the MoO₄²⁻-H₂O₂, NH₃-MoO₄²⁻-H₂O₂ and NaOH-MoO₄²⁻-H₂O₂ decontaminants was 60.49 kJ·mol⁻¹, 39.41 kJ·mol⁻¹ and 44.00 kJ·mol⁻¹, respectively, which showed the reaction rate of PhSMo in the MoO₄²⁻-H₂O₂ decontaminant was more seriously affected by temperature than that in NH₃-MoO₄²⁻-H₂O₂ and NaOH-MoO₄²⁻-H₂O₂ decontaminants.

This was also reflected in the change relations of the reaction rate constants k in the three decontaminants at the same temperature. At -10 °C, rate constants k of PhSMo was obviously higher in the MoO₄²⁻-H₂O₂ decontaminant (1.28 min⁻¹) than that in NH₃-MoO₄²⁻-H₂O₂ (0.82 min⁻¹) and NaOH-MoO₄²⁻-H₂O₂ (0.49 min⁻¹). While at -25 °C, rate constants k of PhSMo was less in the MoO₄²⁻-H₂O₂ decontaminant (0.23 min⁻¹) than that in NH₃-MoO₄²⁻-H₂O₂ (0.27 min⁻¹).

The difference in the apparent reaction rate constant k at the same temperature may be mainly due to the effect of the modified decontaminants on the pH. The pH values of the MoO₄²⁻-H₂O₂, NH₃-MoO₄²⁻-H₂O₂ and NaOH-MoO₄²⁻-H₂O₂ were 6.4, 8.9 and 9.0, respectively. With the addition of inorganic alkaline, the alkalinity of the decontaminants was improved, but the oxidation electrode potential of the system was reduced, which reduced the rate of the primary oxidation reaction. At the same time, the addition of inorganic alkaline also changed the kinetic

mechanism of the reaction, resulting in a slight decrease in E_a , which reduced the sensitivity of the reaction rate to temperature.

4 Conclusion

Results showed that the reaction rate constants k decreased with the increase of pH in both NH₃ and NaOH modified MoO₄²⁻-H₂O₂ at -20 °C, and the relative ratio of sulfone to sulfoxide increased especially when pH was more than 9. The E_a of PhSMo oxidation in the alkaline-modified MoO₄²⁻-H₂O₂ decontaminants was lower than that in the MoO₄²⁻-H₂O₂ decontaminant, which indicated that the sensitivity of the oxidation reaction rate to temperature in MoO₄²⁻-H₂O₂ was reduced after modification.

Hence, compared with MoO₄²⁻-H₂O₂ decontaminant, the oxidation of the alkali-modified decontaminants was slightly lower due to the increase of alkalinity, but the sensitivity of the oxidation reaction rate to temperature was obviously reduced, especially for NH₃-modified decontaminant. It provided a formula design idea for further development and design of decontaminations with both oxidation and nucleophilic properties, which was suitable for subzero environment.

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