Oxidation of Methanethiol and Dimethyl Sulfide in Exhaust Gas by Sodium Hypochlorite Solution

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ABSTRACT

Methanethiol and dimethyl sulfide were absorbed and oxidized with sodium hypochlorite solutions, whereby the overall mass transfer coefficients \((K_Ga)\) were examined. The optimum conditions for oxidizing 5 ppm of methanethiol and 5 ppm of dimethyl sulfide at a room temperature were clarified. On the basis of the data obtained, oxidative deodorization of methanethiol and dimethyl sulfide in real exhaust gas from a night soil plant was tested by using a practical oxidation plant.

INTRODUCTION

Malodorous gas from sewage, night soil or refuse treatment plants contains hydrogen sulfide, methanethiol, dimethyl sulfide and the like as malodorous components, which often cause environmental pollution problems. How to eliminate hydrogen sulfide from malodorous gas was the subject of our earlier paper\(^1\). Oxidative treatment of methanethiol and dimethyl sulfide with sodium hypochlorite has been investigated in this paper. Although oxidation of methanethiol and dimethyl sulfide with sodium hypochlorite has been already reported by some authors\(^2\)–\(^9\), little is known about the oxidation conditions applicable to practical deodorization. With a view of finding out the optimum conditions for practical deodorization, absorptive oxidation of methanethiol and dimethyl sulfide with sodium hypochlorite solutions has been experimented using a packed tower, whereby the overall mass transfer coefficients \((K_Ga)\) have been calculated.

EXPERIMENTAL

Reagent and equipment

All the reagents used were of the special grade, except sodium hypochlorite of industrial grade (available chlorine: 12%). Cylinder-confined methanethiol (purity: 98.5%) and dimethyl sulfide (purity: 98.0%) were used. A Shimazu gas chromatograph (GC-4BFF) and a Hitachi-Horiba pH meter (M-7) were used. A packed tower made of transparent polyvinyl chloride was of 80 mm in diameter and was packed with Takiron packings.

Procedure and analysis

Absorptive oxidation of methanethiol and dimethyl sulfide was carried out by the flow as shown in Fig. 1. Sample gas was sent by a blower from the lower part and the absorptive solution was sprinkled from the upper onto the packings, being contacted with gas in counter current. Sodium hypochlorite was determined by iodometry and methanethiol, dimethyl sulfide and dimethyl disulfide were determined by gas chromatography (FPD).

RESULTS AND DISCUSSION

Influence of pH and liquid flow rate on the overall mass transfer coefficients \((K_Ga)\)

Factors affecting \(K_Ga\) \((\text{kg-mol/m}^3\cdot\text{h} \cdot \text{atm})\) were investigated by absorbing and oxidizing methanethiol and dimethyl sulfide with a sodium hypochlorite solution at a room temperature. \(K_Ga\) was calculated by the following equation\(^3\), assuming the equilibrium pressure to be 0:

\[
K_Ga = \frac{G_m}{P_H \ln \frac{y_1}{y_2}} \quad (1)
\]

\(G_m\): superficial molar velocity of gas \((\text{kg-mol/m}^3\cdot\text{h})\)

\(H\): height of packing tower \((\text{m})\)

\(y_1, y_2\): concentration of gas at the inlet and outlet
of the packed tower (mole fraction)

\( P = \text{total pressure (atm)} \)

Firstly, in order to clarify the influence of pH on \( K_{Ga} \) in the \( CH_3SH\)-Air-NaOCl and \( CH_3SCH_3\)-Air-NaOCl systems, methanethiol (4-5 ppm) and dimethyl sulfide (4-5 ppm) were absorbed and oxidized by the procedure above described, with a sodium hypochlorite solution (1.2 \( \times 10^{-2} \) mol/l), adjusted in the pH range of 9-12 (for the \( CH_3SH\)-Air-NaOCl system) and of 7-13 (for the \( CH_3SCH_3\)-Air-NaOCl system). The packed height was 60 cm. The gas flow rate was set 40 kg/h (superficial gas velocity: 1.7 m/s) and the liquid flow rate was set at 80 kg/h (liquid/gas ratio: 2). The results obtained are shown in Fig. 2. As shown in Fig. 2, \( K_{Ga} \) in the \( CH_3SH\)-Air-NaOCl system increased with the rise of pH value of the absorptive solution, reaching 870 at pH 9, 1,150 at pH 10, 1,550 at pH 11 and 2,613 at pH 12, respectively. This is probably attributable to the promotion of the following reactions with the rise of pH value.

\[
\begin{align*}
\text{CH}_3\text{SH} + \text{NaOH} &= \text{CH}_3\text{SNa} + \text{H}_2\text{O} \quad \text{(2)} \\
2\text{CH}_3\text{SNa} + \text{NaOCl} + \text{H}_2\text{O} &= \text{CH}_3\text{SSCH}_3 + 2\text{NaOH} + \text{NaCl} \quad \text{(3)}
\end{align*}
\]

However, \( K_{Ga} \) tended to decrease gradually in the pH range above 10, since insoluble carbonate was formed in the absorptive solution under the influence of carbon dioxide gas in the air, depositing in the tower as scale, on the occasion of long run. Therefore, pH value of around 10 seems to be suitable, in spite of rather small \( K_{Ga} \) value, where 94% of removal rate was guaranteed.

Stripping of dimethyl disulfide was hardly observed in any pH range. Figure 2 shows that \( K_{Ga} \) in the \( CH_3SCH_3\)-Air-NaOCl system decreases with the rise of its pH value, reaching 1,745 at 9, 1,599 at 10, 1,082 at 11, 176 at 13. This can be ascribed to the heavy dependence of the following reaction on pH (11, 12 and 13).

\[
\text{CH}_3\text{SCH}_3 + \text{NaOCl} = \text{CH}_3\text{SOCH}_3 + \text{NaCl} \quad \text{(4)}
\]

Thus, although \( K_{Ga} \) was larger in a low range of pH of the absorptive solution, pH value of around 10 seems to be suitable since chlorine odor becomes sensible at lower pH values than 9.

Next, in order to clarify the influence of the liquid flow rate, a comparative test was carried out by changing it from 40 kg/h to 120 kg/h and setting the gas flow rate at 40 kg/h and pH at around 10. \( K_{Ga} \) in the both systems of \( CH_3SH\)-Air-NaOCl and \( CH_3SCH_3\)-Air-NaOCl became gradually larger with the increase of liquid flow rate, reaching 890 and 1,300 at 40 kg/h, respectively. At higher rate than 80 kg/h, however, \( K_{Ga} \) in the both systems remained almost unchanged (1,550, 1,599, respectively), although slight increase was observed. Consequently, the liquid flow rate of 80 kg/h (liquid/gas ratio: 2) seems to be suitable. Under these conditions, the temperature effect was hardly observed.

**Influence of the concentration of sodium hypochlorite (molar ratio)**

In order to examine the influence of sodium hypochlorite concentration on \( K_{Ga} \) in the both
Fig. 3 Influence of the sodium hypochlorite concentration on $K_{Ga}$.

gas flow rate: 40 kg/h  
liquid flow rate: 80 kg/h  
packed height: 60 cm  
pH : 10, temperature : 28°C,  

$\bullet$ : CH$_3$SCH$_3$ (5 ppm)  
$\bigcirc$ : CH$_3$SH (5 ppm)

These results suggest that proper concentration of sodium hypochlorite, at which 5 ppm of methanethiol and/or 5 ppm of dimethyl sulfide can be treated almost completely, is $1.2 \times 10^{-2}$ mol/l (molar ratio of NaOCl/CH$_3$SH: $1.4 \times 10^2$, that of NaOCl/CH$_3$SCH$_3$: $1.4 \times 10^3$).

**Influence of sodium chloride formed**

The concentration of sodium chloride formed in the absorptive solution became gradually high, when the solution was repeatedly used in circulation. Then, the influence of sodium chloride formed was examined using sodium hypochlorite solutions ($1.2 \times 10^{-2}$ mol/l) added with sodium chloride by 2.0, 4.0, 6.0, and $8.0 \times 10^{-1}$ mol/l, respectively, at 40 kg/h of the gas flow rate, 80 kg/h of the liquid flow rate and pH 10. The results are shown in Fig. 4, from which the following can be concluded. $K_{Ga}$ in the both systems of the CH$_3$SH-Air-NaOCl and CH$_3$SCH$_3$-Air-NaOCl tended to decrease so slightly that the concentration of sodium chloride was almost insignificant. However, since at the concentrations examined, pH value of the absorptive solution is sensitive to move, the sodium chloride concentration is desirable to be lower than $8.0 \times 10^{-1}$ mol/l.

**Deodorizing effect of malodorous gas from an actual plant**

Malodorous gas from an actual night soil treatment (aerobic oxidation) plant was submitted to the deodorizing test under the following oxidation conditions:

- Gas flow rate to be treated: 720 m$^3$/min
- Superficial gas velocity: 1.7 m/s
- Liquid/gas ratio: 2
- Packed height: 180 cm (2” Takiron packings)
- pH of the absorptive solution: 9.5–10.0
- Concentration of sodium hypochlorite in the absorptive solution: $9.0 \times 10^{-3}$ mol/l.
- Supply water flow rate: 18 l/min.
- Sample gas accompanied hydrogen sulfide. But, ammonia and trimethylamine in it were removed in advance with a hydrochloric acid solution, as shown by the flow sheet in Fig. 5. Table 1 shows the results, presenting the removal rate of 97% with both regards to methanethiol and dimethyl sulfide.
Fig. 5 Flow sheet of practical oxidation plant.
1. blower, 2. packed tower (for NH₃ and (CH₃)₃N), 3. packed tower (for CH₃SH and CH₃SCH₃), 4. tank, 5. pump

Table 1. Deodorizing effect of malodorous gas from an actual night soil treatment plant

<table>
<thead>
<tr>
<th>Run</th>
<th>Malodorous component</th>
<th>Concentration (ppm)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inlet</td>
<td>Outlet</td>
</tr>
<tr>
<td>1</td>
<td>CH₃SH</td>
<td>0.98</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>CH₃SCH₃</td>
<td>0.58</td>
<td>0.019</td>
</tr>
<tr>
<td>2</td>
<td>CH₃SH</td>
<td>1.68</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td>CH₃SCH₃</td>
<td>1.40</td>
<td>0.043</td>
</tr>
</tbody>
</table>

**CONCLUSION**

Methanethiol and dimethyl sulfide were absorbed and oxidized with sodium hypochlorite solutions, whereby the overall mass transfer coefficients (Kᵮ arquivo) were examined. The following optimum conditions for oxidizing 5 ppm of methanethiol and 5 ppm of dimethyl sulfide at a room temperature were clarified; liquid/gas ratio: 2 (liquid flow rate: 80 kg/h) at the superficial gas velocity of 1.7 m/s (gas flow rate: 40 kg/h), pH of the absorptive solution: around 10, concentration of sodium hypochlorite in the absorptive solution: 1.2 × 10⁻² mol/l (molar ratio of NaOCl/CH₃SH: 1.4 × 10² and that of NaOCl/CH₃SCH₃: 1.2 × 10³). On these conditions, methanethiol and dimethyl sulfide in malodorous gas could be removed almost completely.

**REFERENCES**