Extractive Removal of Formaldehyde by Using an Imination Reaction with a Trident Amine Type Molecule

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Dedicated to Mr. Ayahiro Yamashita.

Extractive removal of harmful formaldehyde and ketone compounds by using an imination reaction with a trident amine derivative has been investigated. Removal of formaldehyde was quantitatively achieved over the whole pH range examined from 2 to 9 within 2 h. Although the regeneration of the compound was not adequate due to elution of the compound and incomplete reverse reaction, the removal was effective and the imination reaction took place quantitatively.

1. Introduction

Formaldehyde, the simplest aldehyde, is a colorless gas that has an irritating odor. It has been employed as a precursor for many commercial resins and polymers for adhesive and coating materials, together with synthetic compounds and polyfunctional alcohols. Formalin, in its commercial form, is also useful for disinfectants, biocides and embalming reagents. Although formaldehyde has been extensively employed and is generated even in the human body, exposure to large amounts causes health damage to humans due to its toxicity such as irritation of the skin and eyes, leukemia, cancers. Its use has been controlled, and its safe removal has been required based on international or regional controls. Various approaches to decompose, remove and detect formaldehyde have been reported by using plasma [1], inorganic catalysts [2,3], organic adsorbents [4], and by sensor monitoring [5]. Recently, adsorbents functionalized with amine compounds have been reported for reactive removal of such aldehydes [6-8], while extractive removal of formaldehyde with amine compounds has not been reported, although the imination reaction of aldehydes and amines is well-known.

Various types of extraction reagents, metal adsorbents, ion-selective electrodes based on macrocyclic calixarenes have been prepared [9-12] for metal separation and detection in our group. This work has been reviewed [13-16]. Recently, “trident molecules”, pseudomacrocyclic tripodal alkyl trimethylol derivatives have also been prepared to investigate extraction [17-20] and ion-sensing [21] behavior. The trident molecules provide the following characteristics, that is, easy availability of the alkyltrimethylols from the corresponding aldehydes and formaldehyde, possessing three alcoholic hydroxyl groups for modification to a tridentate ligand with C₃ symmetry, a relatively narrow coordination site for size discrimination, and high
coordination ability due to the chelating effect and converging effects of multifunctionality [17]. The trident molecules possess tripods to trap plural molecules and ions. When the molecule is well designed, it can trap both catalytic metal ions and hazardous aldehydes in a single molecule and its metal complex can decompose the trapped aldehydes. A catalytic model of a well-designed trident molecule loading metal ion and the roles of each pod in the tripodal molecule are shown in Figure 1.

In the present study, we report fundamental research on the extractive removal of hazardous carbonyl compounds by the imination reaction with the amino derivative of the trident molecule for its catalytic decomposing properties in future work as shown in Figure 1.

2. Experimental

2.1 Reagents

1,1,1-Tris(aminomethyl)-9-decene (\(\text{CH}_2=\text{CH}((\text{CH}_2)_3\text{NH}_2\)) was prepared through four steps of condensation to make 1,1,1-tris(hydroxymethyl)-9-decene [17, 22, 23], tosylation [24-26], azidation [25-27], and amination [19, 20, 25-27]. Other chemicals were purchased and used without further purification.

The chemical structure for the trident molecule in the present work is shown in Figure 2.

2.2 Elution of the extraction reagent into the aqueous phase

Organic solutions were prepared by diluting \(\text{CH}_2=\text{CH}((\text{CH}_2)_3\text{NH}_2\) as the extraction reagent to 5 mM (M=mol dm\(^{-3}\)) in analytical grade chloroform. The aqueous solution was prepared by mixing 0.1 M hydrochloric acid, 0.1 M HEPES (2-[4-(2-hydroxyethyl)-1-piperaziny]ethanesulfonic acid) as a buffer solution, and 0.1 M sodium hydroxide solution. Both solutions were mixed to adjust the pH. Equal volumes (5 cm\(^3\)) of both phases were mixed and shaken at 303 K for more than 2 h. After phase separation, the concentration of \(\text{CH}_2=\text{CH}((\text{CH}_2)_3\text{NH}_2\) concentration in the organic phase was measured by means of an ultraviolet-visible spectrophotometer (Hitachi, UV-VIS U-3310) at 240 nm, the wavelength of the \(\pi - \pi^*\) transfer of the unsaturated bond for \(\text{CH}_2=\text{CH}((\text{CH}_2)_3\text{NH}_2\).
2.3 Extractive removal of formaldehyde

Organic solutions were prepared by diluting $^8$None{3}$\text{CH}_2\text{NH}_2$ in analytical grade chloroform to a concentration of 5 mM. Aqueous solutions were prepared by diluting a formaldehyde standard solution (1,000ppm) in 0.1 M hydrochloric acid, 0.1 M HEPES, and 0.1 M sodium hydroxide solutions to the desired concentrations. Three stock solutions were mixed to adjust the pH. Equal volumes (5 cm$^3$) of both phases were mixed and shaken in 138 rpm at 303 K for more than 2 h. After phase separation, the formaldehyde concentration in the aqueous phase was measured by colorimetry for acetic acetone determination (JIS K0102, 29.1) using an ultraviolet-visible spectrophotometer (Hitachi, UV-VIS U-3310). The pH value of the aqueous phase was measured using a pH meter (Orion-720A). The % Removal was defined by

$$\% \text{Removal} = \frac{[\text{HCHO}] - [\text{HCHO}]}{[\text{HCHO}]} \times 100$$

(1),

where [HCHO] and [HCHO] are the formaldehyde concentrations in the aqueous phase before and after the imination reaction.

2.4 Proton nuclear resonance study

The $^1$H-NMR spectra of $^8$None{3}$\text{CH}_2\text{NH}_2$ before and after the imination reaction with formaldehyde were also recorded to check the reaction completion. The extraction procedure was almost the same as that described in 2.3 except for the use of deuterium solvents. After loading, the chloroform was removed in vacuo, then the deuterated chloroform was added to the residue. The spectra were recorded using a $^1$H-NMR spectrometer (Jeol JNM-GX300).

The extractive removal of methyl isobutyl ketone (MIBK) and acetone with $^8$None{3}$\text{CH}_2\text{NH}_2$ was also investigated and checked by $^1$H-NMR spectra using the same procedure.

3. Results and Discussion

3.1 Elution of the extraction reagent into the aqueous phase

The $^8$None{3}$\text{CH}_2\text{NH}_2$ possesses three primary amino groups and one lipophilic nonenyl branch. Since it is easily protonated under acidic conditions, it was expected to distribute into the aqueous phase at low pH. The effect of pH on the percentage elution of $^8$None{3}$\text{CH}_2\text{NH}_2$ into the aqueous phase is shown in Figure 3. The percentage elution of $^8$None{3}$\text{CH}_2\text{NH}_2$ was calculated by

$$\% \text{Elution} = \frac{[^8\text{None}{3}\text{CH}_2\text{NH}_2]_{\text{i}} - [^8\text{None}{3}\text{CH}_2\text{NH}_2]_{\text{e}}}{[^8\text{None}{3}\text{CH}_2\text{NH}_2]_{\text{i}}} \times 100$$

(2),

where $[^8\text{None}{3}\text{CH}_2\text{NH}_2]_{\text{i}}$ and $[^8\text{None}{3}\text{CH}_2\text{NH}_2]_{\text{e}}$ are the initial and equilibrium concentrations of $^8$None{3}$\text{CH}_2\text{NH}_2$ in the organic phase. Although the percentage elution decreased as the pH value, was increased 56.1% and 19.8% percent elution were observed at pH 1.17 and 10.2, and thus the change in the degree of elution was quite small compared to the pH change. From Figure 3, $pK_{a1}$ and $pK_{a2}$ for $^8$None{3}$\text{CH}_2\text{NH}_2$ appear at pH values around 6 - 7 and 8 – 10, respectively. The $pK_a$ values of tris(aminomethyl)ethane which has a with shorter lipophilic branch chain, were reported to be 10.4, 8.6, and 5.8 [28]. The present $pK_{a1}$ and $pK_{a2}$ values for the longer lipophilic branch compound,
$^8$None$\text{\{}3\text{}\}CH_2NH_2$, seem to almost correspond with those for the shorter one.

Although the elution of $^8$None$\text{\{}3\text{}\}CH_2NH_2$ into the aqueous phase was not negligible, since $^8$None$\text{\{}3\text{}\}CH_2NH_2$ becomes more lipophilic after the imination reaction, further investigation was carried out.

3.2 Extractive removal of formaldehyde

The effect of the reaction time on the percentage removal of formaldehyde with $^8$None$\text{\{}3\text{}\}CH_2NH_2$ is shown in Figure 4. The percentage removal became constant, at 62% within a reaction time of 2 h under the present conditions. The shaking rate was moderate and adjusted to 138rpm. The reaction seemed to be quite quick. Because of the hydrophilicity of $^8$None$\text{\{}3\text{}\}CH_2NH_2$, the imination reaction can take place even in the aqueous phase. However, it would take longer for the formaldehyde to react with the protonated primary amino groups. The reaction time hereafter was adjusted to 48 h. The 62% removal seemed to be meaningful. The phase ratio was 1 to 1. The concentrations of $^8$None$\text{\{}3\text{}\}CH_2NH_2$ and formaldehyde were 5 and 20 mM in this experiment. The $^8$None$\text{\{}3\text{}\}CH_2NH_2$ provides three amino groups. Thus, after complete reaction, 5 mM formaldehyde should remain and the percentage removal should be 75%. Therefore, the present imination reaction definitely took place and the percentage removal of formaldehyde with $^8$None$\text{\{}3\text{}\}CH_2NH_2$ was very effective.

![Figure 3](image1.png)  
**Figure 3.** Effect of pH on the percentage elution of $^8$None$\text{\{}3\text{}\}CH_2NH_2$ into the aqueous phase. $[^8\text{None}\{3\}\text{CH}_2\text{NH}_2] = 5 \text{ mM}, 0.1 \text{ M HCl} - 0.1 \text{ M HEPES solution} - 0.1 \text{ M NaOH solution}, 303 \text{ K}, 48 \text{ h shaking}.$

![Figure 4](image2.png)  
**Figure 4.** Effect of the reaction time on the percentage removal of formaldehyde with $^8$None$\text{\{}3\text{}\}CH_2NH_2$. $[^8\text{None}\{3\}\text{CH}_2\text{NH}_2] = 5 \text{ mM}, [\text{formaldehyde}] = 20 \text{ mM}, \text{pH} = 9.0 \text{ (0.1 M HEPES solution} - 0.1 \text{ M NaOH solution), 303 K, 48 h shaking}.$

The effect of pH on the percentage removal of formaldehyde with $^8$None$\text{\{}3\text{}\}CH_2NH_2$ is shown in Figure 5. The percentage removal of formaldehyde was almost quantitative, although a slight decrease was observed at lower pH values due to protonation and transfer of $^8$None$\text{\{}3\text{}\}CH_2NH_2$ into the aqueous phase. The concentrations of $^8$None$\text{\{}3\text{}\}CH_2NH_2$ and formaldehyde were adjusted to be 5 and 10 mM in this experiment. The amount of the primary amino groups in $^8$None$\text{\{}3\text{}\}CH_2NH_2$ was in excess of that of formaldehyde. The result of the pH dependency also supported that the imination reaction took place and
the percentage removal was very good.

The effect of the initial formaldehyde concentration on the percentage loading on $^{8}$None{3}CH$_2$NH$_2$ on the degree of formation of the imino compound is shown in Figure 6. The percentage loading of formaldehyde on $^{8}$None{3}CH$_2$NH$_2$ was calculated by

$$%Loading = \frac{[HCHO]_i - [HCHO]_e}{[^{8}\text{None}{3}CH_2NH_2]_i} \times 100$$

where $[^{8}\text{None}{3}CH_2NH_2]_i$, $[HCHO]_i$, and $[HCHO]_e$, are the initial concentrations of $^{8}$None{3}CH$_2$NH$_2$ in the organic phase and formaldehyde in the aqueous phase before and after the reaction.

The percentage loading approached 270%. Since more than 20% of $^{8}$None{3}CH$_2$NH$_2$ can be transferred to the aqueous phase from the result shown in Figure 3, the percentage loading was sufficiently high and the stoichiometry of the imination reaction was readily estimated to be 1 : 3 ($^{8}$None{3}CH$_2$NH$_2$ to formaldehyde). The imination reaction was almost quantitative.

The effect of hydrochloric acid concentration on the percentage recovery of formaldehyde from formaldehyde-loaded $^{8}$None{3}CH$_2$NH$_2$ is shown in Figure 7. The percentage recovered of formaldehyde was calculated by

$$%Recovery = \frac{[HCHO]_e}{[^{8}\text{None}{3}CH_2NH_2]_i} \times 100$$

Figure 5. Effect of pH on the percentage removal of formaldehyde with $^{8}$None{3}CH$_2$NH$_2$. $[^{8}$None{3}CH$_2$NH$_2] = 5$ mM, [formaldehyde] = 10 mM, 0.1 M HCl - 0.1 M HEPES solution - 0.1 M NaOH solution, 303 K, 48 h shaking.

Figure 6. Effect of the initial formaldehyde concentration on the percentage loading on $^{8}$None{3}CH$_2$NH$_2$. $[^{8}\text{None}{3}CH_2NH_2] = 5$ mM, pH = 9.0 (0.1 M HEPES solution - 0.1 M NaOH solution), 303 K, 48 h shaking.

Figure 7. Effect of hydrochloric acid concentration on the percentage recovery of formaldehyde from formaldehyde-loaded $^{8}$None{3}CH$_2$NH$_2$. [formaldehyde-loaded $^{8}$None{3}CH$_2$NH$_2] = 5$ mM, 0.1 – 5.0 M HCl solution, 303 K, 48 h shaking.
%Recovered = \frac{[HCHO]_e}{[HCHO]_{\text{loaded}}} \times 100 \tag{4},

where \([HCHO]_{\text{loaded}}\) and \([HCHO]_e\) are the loaded concentration of formaldehyde on \(^8\)None\{3\}CH\(_2\)NH\(_2\) in the organic phase and the equilibrium concentration of formaldehyde in the aqueous phase, respectively. The percentage recovery of formaldehyde from formaldehyde-loaded \(^8\)None\{3\}CH\(_2\)NH\(_2\) was only 40% due to the stability of the aldimino compound.

### 3.3 Proton nuclear resonance study

The \(^1\)H-NMR spectra of \(^8\)None\{3\}CH\(_2\)NH\(_2\) before and after the imination reaction were recorded to confirm the reaction of formaldehyde with \(^8\)None\{3\}CH\(_2\)NH\(_2\). The \(^1\)H-NMR spectra of \(^8\)None\{3\}CH\(_2\)NH\(_2\) before and after the imination reaction are shown in Figure 8. The singlet peak of methylene protons next to the amino groups disappeared and shifted from 2.59 to 3.24ppm as a new singlet peak. New peaks appeared at 4.12 and 4.48ppm as double doublet peaks. They were derived from two methylene imine protons (-N=CH\(_2\)) with different environments. These peak shifts and the new peaks strongly supported the formation of the imino compound as follows;

\[ R-NH_2 + HCHO \rightleftharpoons R-N = CH_2 + H_2O \tag{5}. \]

Ketonic compounds also react with primary amines to form imino compounds as follows;

\[ R-NH_2 + R'-C(=O) \rightleftharpoons R'-C(=NR) - R'' + H_2O \tag{6}. \]

The \(^1\)H-NMR spectra of \(^8\)None\{3\}CH\(_2\)NH\(_2\) before and after the imination reaction with MIBK and acetone are shown in Figures 9 and 10. Although the new peaks in both spectra after the imination reaction were not identified, they were obviously different from those of the original spectra before the reaction of \(^8\)None\{3\}CH\(_2\)NH\(_2\) due to the instability of the imino compounds formed and the incomplete imination reaction. The singlet peak of the methylene protons next to the amino groups at 2.59ppm disappeared. The amino compound, \(^8\)None\{3\}CH\(_2\)NH\(_2\), also effectively removed the ketonic compounds.

Figure 8. \(^1\)H-NMR spectra of \(^8\)None\{3\}CH\(_2\)NH\(_2\) before and after formaldehyde loading. \([8\text{None}\{3\}CH\(_2\)NH\(_2\}] = 5 \text{ mM}, \ [\text{formaldehyde}] = 50 \text{ mM}, \ \text{pH} = 9.0 \ (0.1 \text{ M HEPES solution} - 0.1 \text{ M NaOH solution}), 303 \text{ K}, 48 \text{ h shaking}.$
4. Conclusion

Extractive removal of hazardous carbonyl compounds, formaldehyde, methyl isobutylketone, and acetone by using an imination reaction with an amine derivative of nonenyltrimethylol has been investigated in this work. Removal of formaldehyde was quantitatively achieved over the whole pH range examined from 2 to 9 within 2 h. Although the regeneration of the compound was not complete even with a high concentration of hydrochloric acid due to the elution of the compound and an incomplete reverse reaction, the removal of such compounds was effective and the imination reaction took place quantitatively.

References