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Leading Innovation >>>

Study on Reaction Mechanisms of Amine Absorbent and Aldehydes

TOSHIBA Corporation,
Corporate Research and Development Center

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Regina, 8th Sept. 2015

Outline

- **Introduction**
- **Experimental**
  - Quantitative analysis of aldehydes
  - Qualitative analysis of reaction products
- **Results and Discussions**
  - Reaction mechanism of amines and aldehydes
    - Primary amine
    - Secondary amines
    - Tertiary amines
- **Summary**

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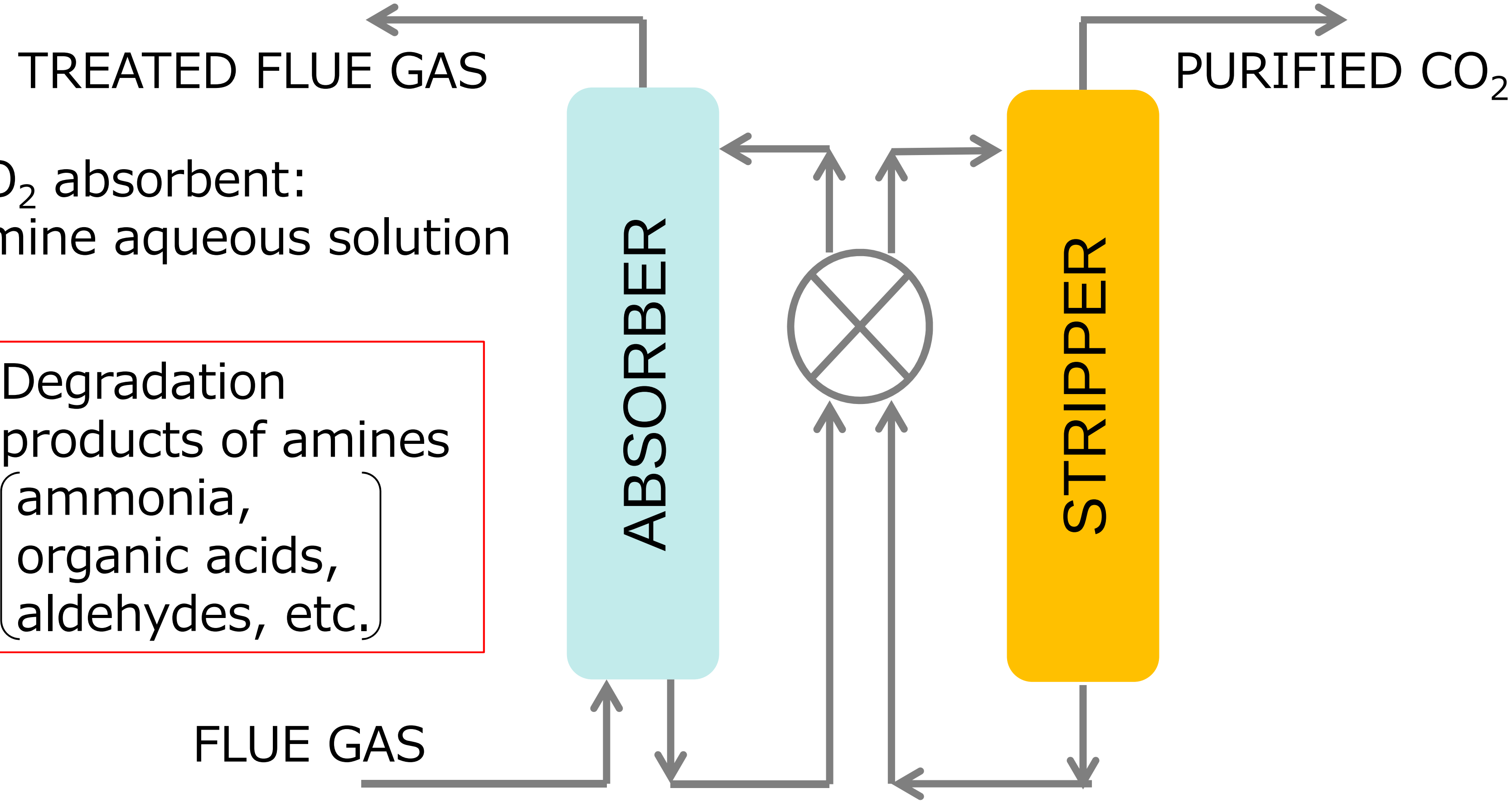
Background of this Study

Process flow diagram for CO_2 capture



CO_2 absorbent:
Amine aqueous solution

Degradation products of amines (ammonia, organic acids, aldehydes, etc.)

Background of this Study

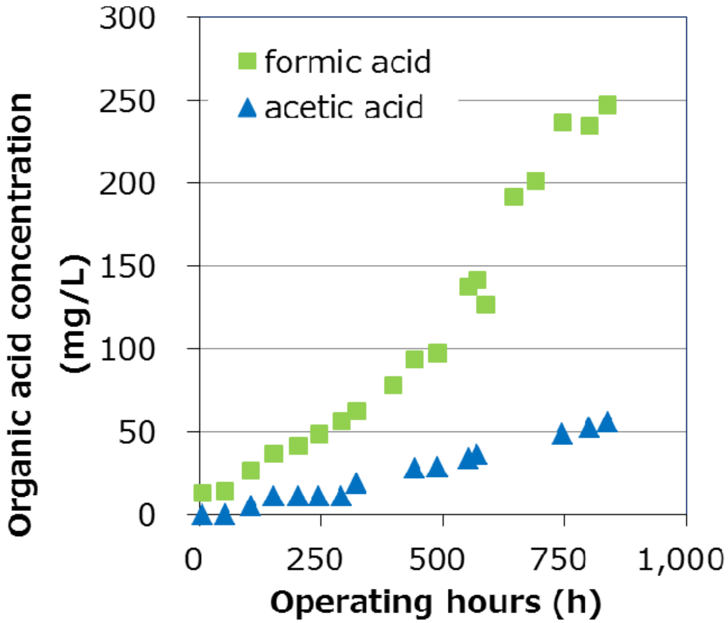
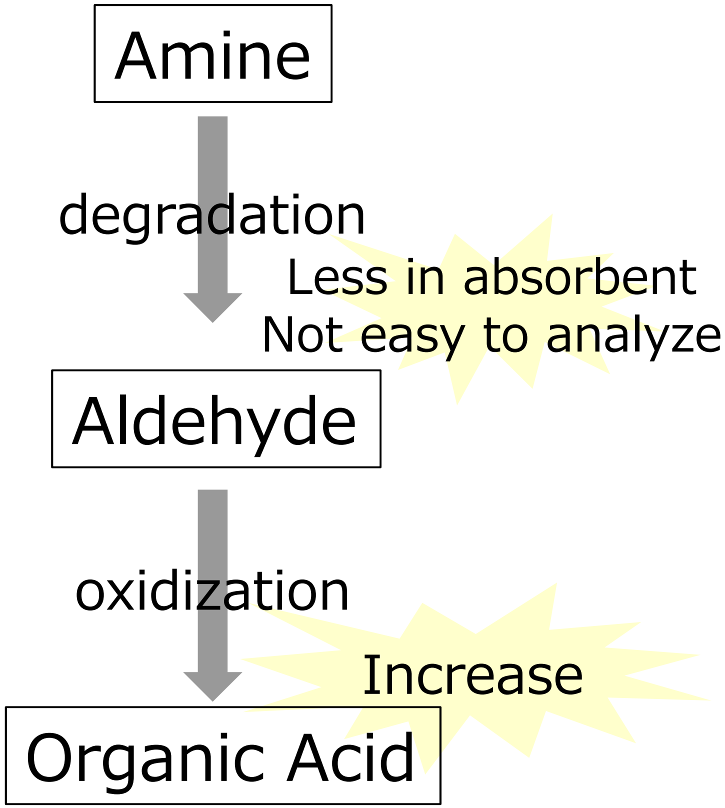


Fig. Increase in concentration of organic acid in absorbent during operation
Ref. S. Saito, *Energy Procedia*, **51,** 176(2014)



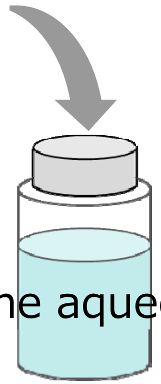
In this study, we describe specific reaction mechanisms of amines and aldehydes.

Research on the reactivity of amines and aldehydes

Table Amines used in this study

Amine Function	Abbreviation	Amine compound
Primary amine	MEA	Monoethanol amine
Secondary amines	DEA	Diethanol amine
	MAE	Methyl amino ethanol
	PZ	Piperazine
Tertiary amines	TEA	Triethanol amine
	DMAE	Dimethyl amino ethanol
	MDEA	Methyl diethanol amine

acetaldehyde



50 g/L amine aqueous solution

0.2 g/L and 10 g/L acetaldehyde solution in amine aqueous solution was prepared.

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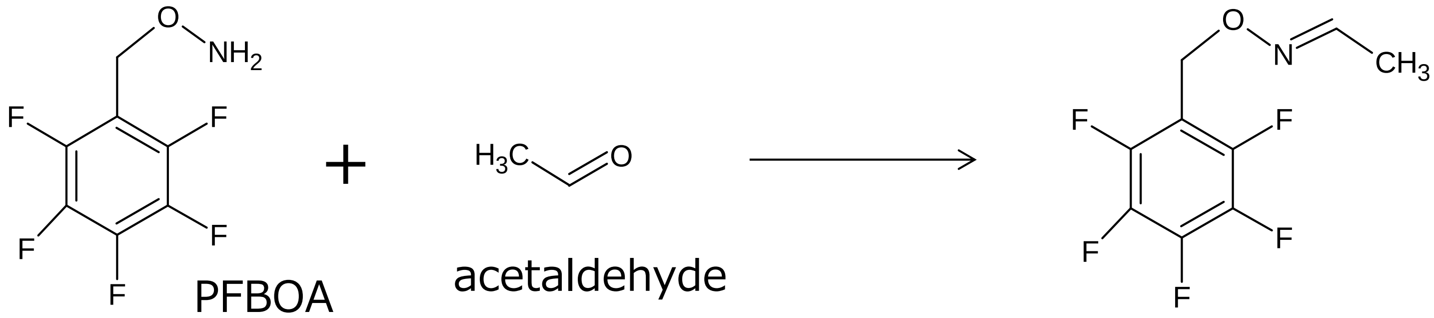
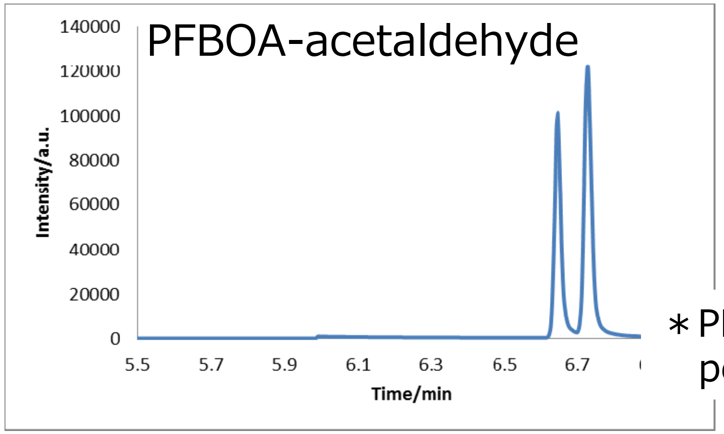
Quantitative analysis method for acetaldehyde derivatized by PFBOA

Aldehydes were derivatized by O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA), and the derivatives were extracted with n-hexane before determination by GC/MS as aldoximes.

Derivatization of acetaldehyde using PFBOA





＊PFBOA-acetaldehyde shows two peaks due to geometric isomer.

Recovery amount of aldehydes in MEA aqueous solution

Table Recovery amount of aldehyde in MEA

Sample	Addition amount of aldehyde	Reaction time *1 of amine and aldehyde	Derivatization pH	Recovery of acetaldehyde (%)
Water	0.2 g/L	-	*2	100
MEA (50g/L)	0.2 g/L	10 min	Weak-acid	106
		10 min	Weak-basic	60
		7 days	Weak-acid	102
		7 days	Weak-basic	68
	10 g/L	10 min	Weak-acid	95
		3 days	Weak-acid	54

*1 The time period between addition of aldehyde and analysis of recovery amount of aldehyde in amine aqueous solution.

*2 Weak-acid-samples were diluted with water and H_2SO_4, and weak-basic-samples were diluted with only water.

Recovery amounts vary widely
→ Analysis cannot be performed stably
→ Investigation of reaction mechanisms is necessary for stable analysis

Recovery amount of aldehydes in MEA aqueous solution

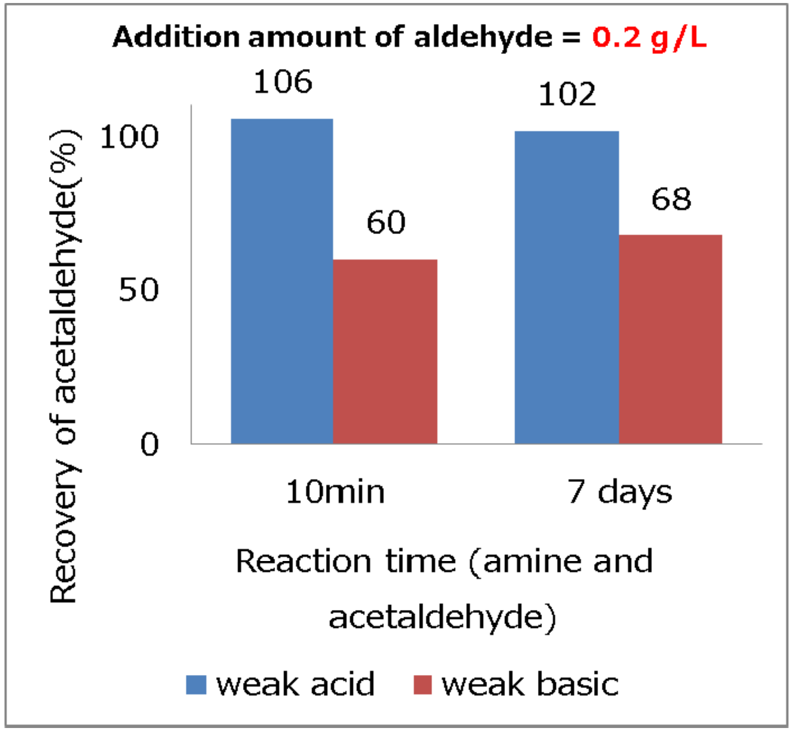
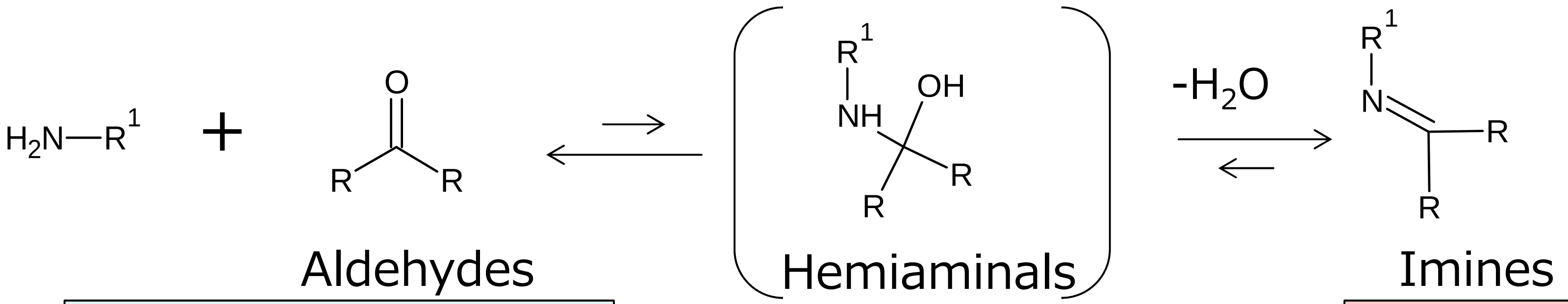


Fig. Recovery amount of aldehyde in MEA

Addition of 0.2g/L acetaldehyde results in
- low recovery amount of aldehyde under basic condition.
- high recovery amount of aldehyde under acid condition.

Reaction mechanisms of primary amines and aldehydes

Reactions of aldehydes and primary amines are reversible, and **aldehydes are formed under acid condition**, generally.



Low pH
(weak acid condition)

High pH
(basic condition)

Ref. Guangtong Wang, *Langmuir.*, **30**, 1531 (2014)

・Under acid condition → Aldehydes are separated from amines.
・Under basic condition → Aldehydes and amines form imines.

All aldehydes which can be separated from amines are analyzed under acid condition.

Recovery amount of aldehydes in MEA aqueous solution

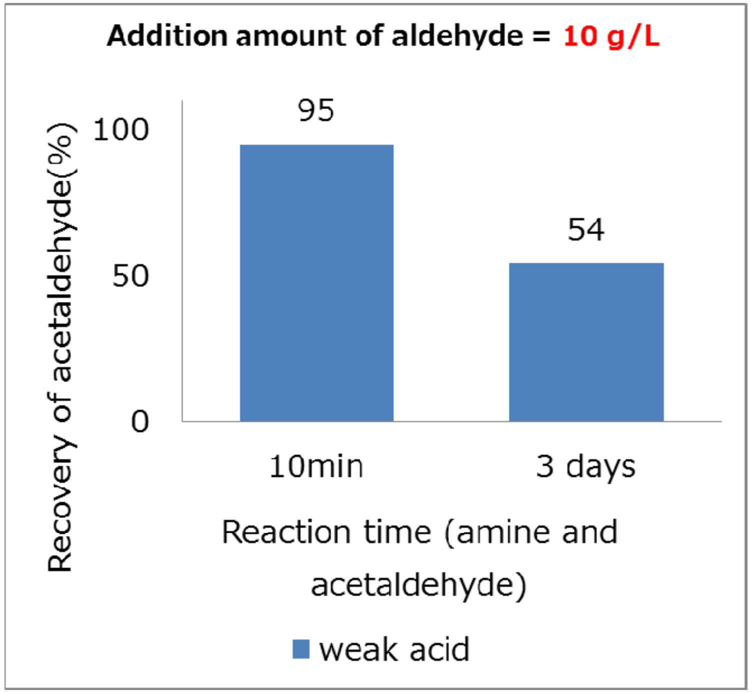
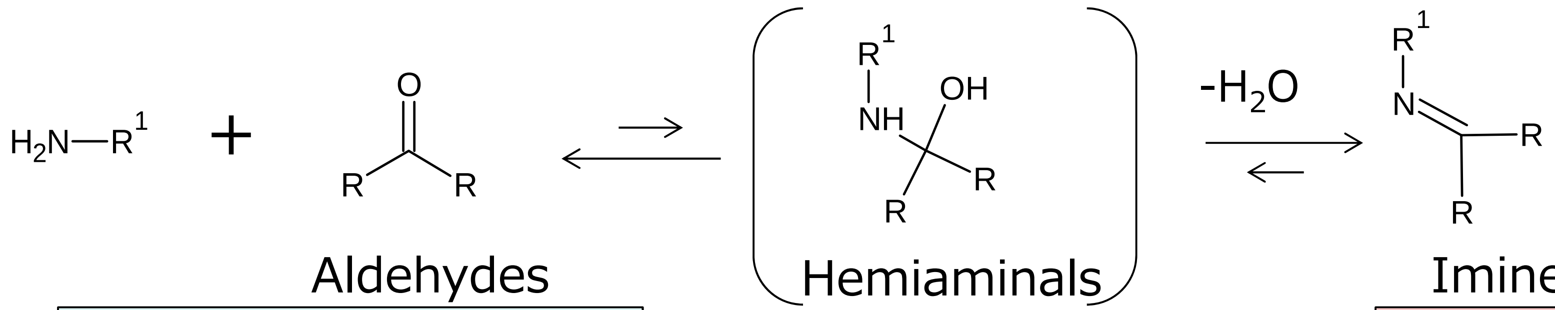


Fig. Recovery amount of aldehyde in MEA

Addition of 10 g/L acetaldehyde and long reaction time results in
・low recovery amount of aldehyde even under acid condition.

Reaction mechanisms of primary amines and aldehydes



Low pH (weak acidic condition)	High pH (basic condition)

Ref. Guangtong Wang, *Langmuir.*, **30**, 1531 (2014)

- Under acidic condition
- Large amount of aldehyde
- Long reaction time

} Low recovery amount of aldehyde

→ Reaction of amine and aldehyde is different from the above scheme.
→ Investigation of reaction products

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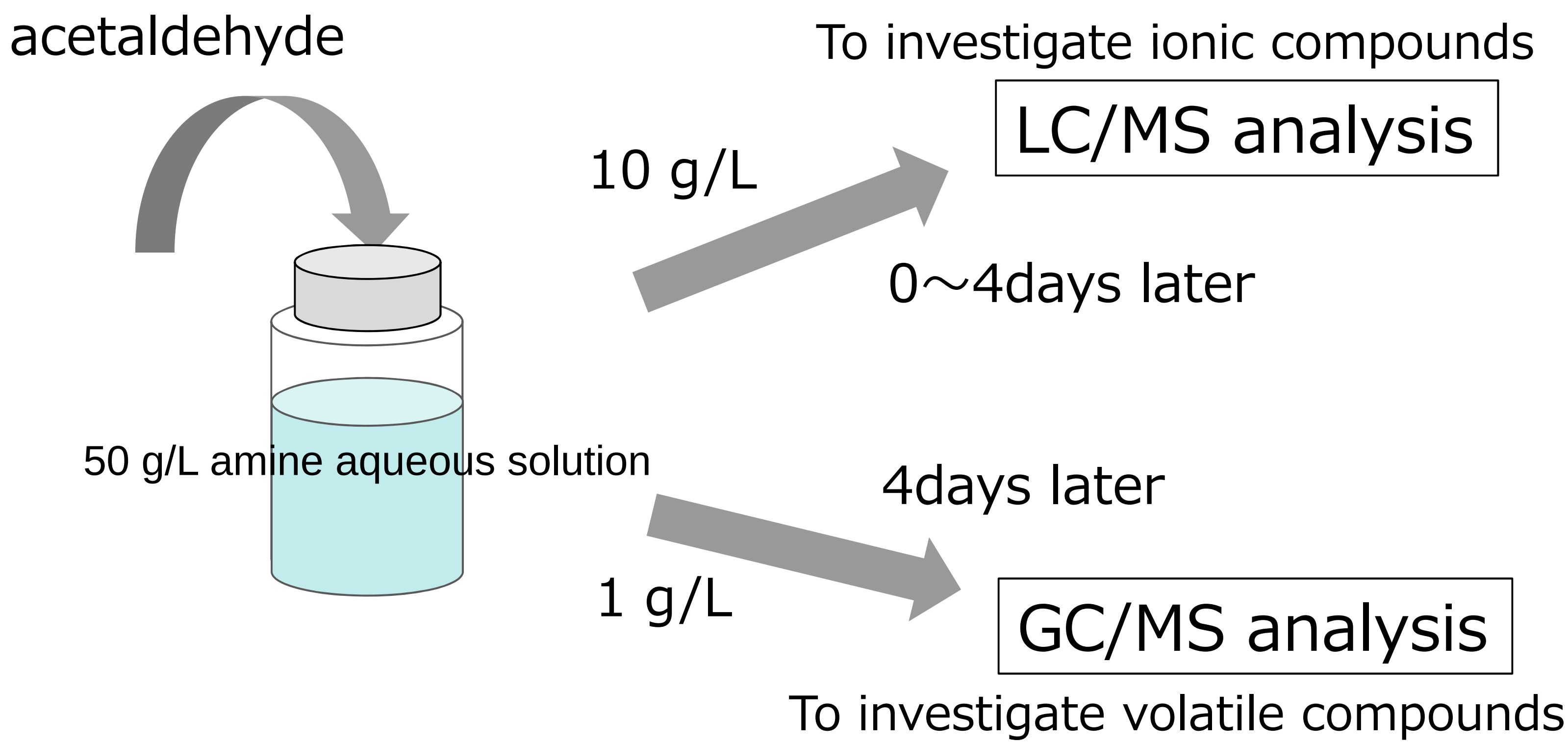
Compounds produced from amines and aldehyde

In order to investigate the products from amines and acetaldehyde, we added acetaldehyde to 50 g/L amine aqueous solution and 1 g/L or 10 g/L acetaldehyde solution was prepared. They were analyzed by LC/MS and GC/MS.



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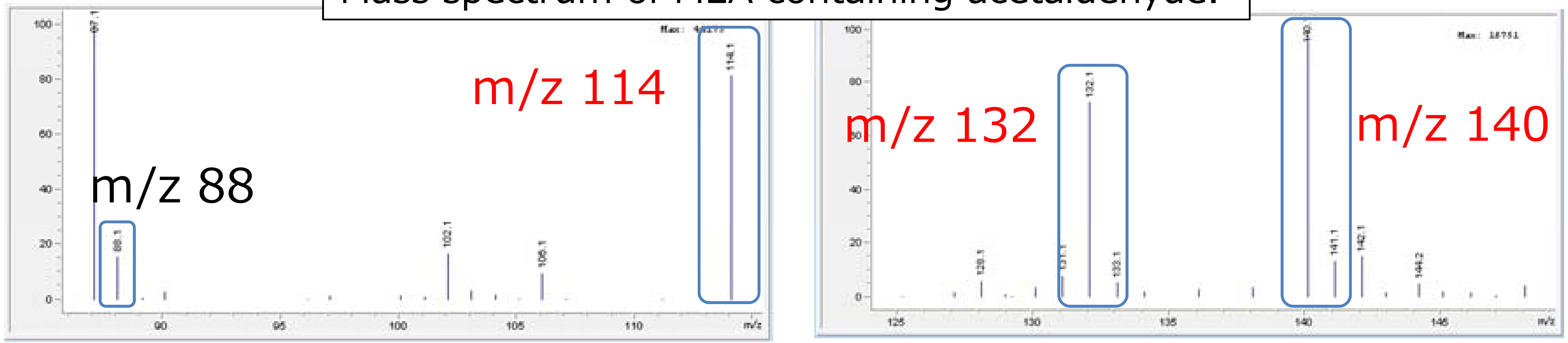
LC/MS analysis of MEA reacted with acetaldehyde

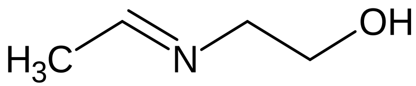
Four days after addition of acetaldehyde

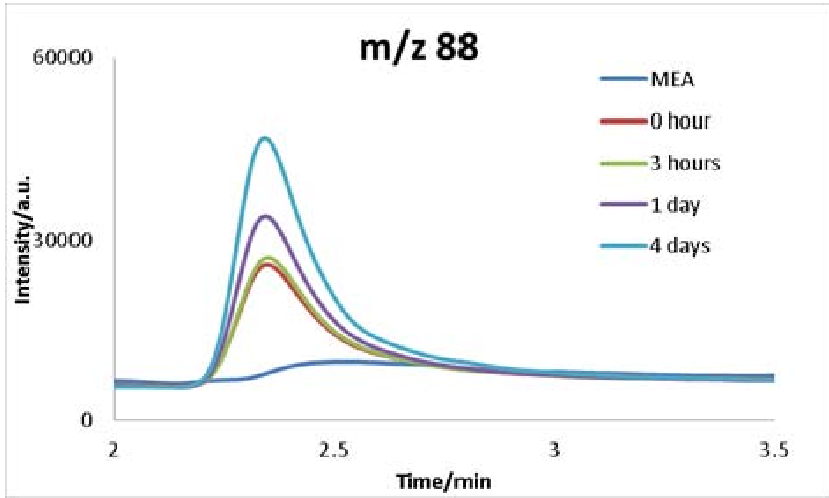
Mass spectrum of MEA containing acetaldehyde.



MS signals of
m/z 88, 114, 132, 140
increased after addition of aldehyde.

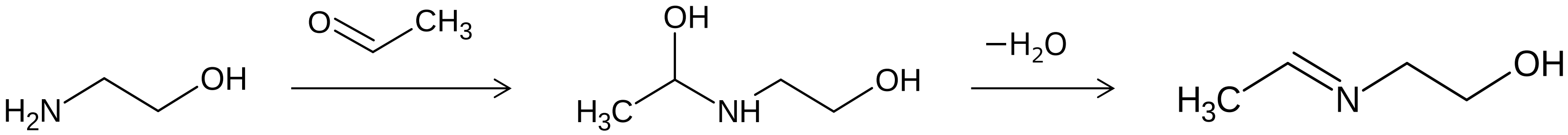
Imine from MEA:m/z 88





Chromatogram of LC/MS

Reaction mechanisms of MEA and acetaldehyde



Mass number 87
(m/z 88)

Imine

Under basic condition

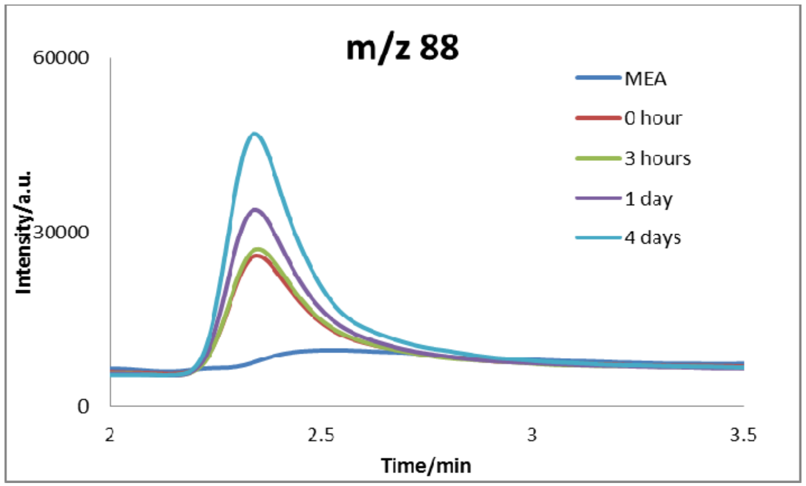
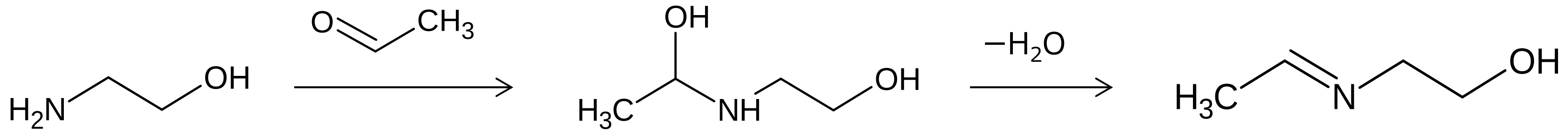


Fig. m/z 88 Chromatogram of LC/MS

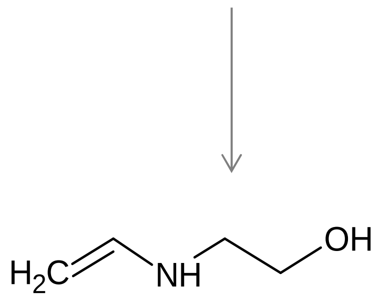
Reaction mechanisms of MEA and acetaldehyde



Mass number 87
(m/z 88)

Imine

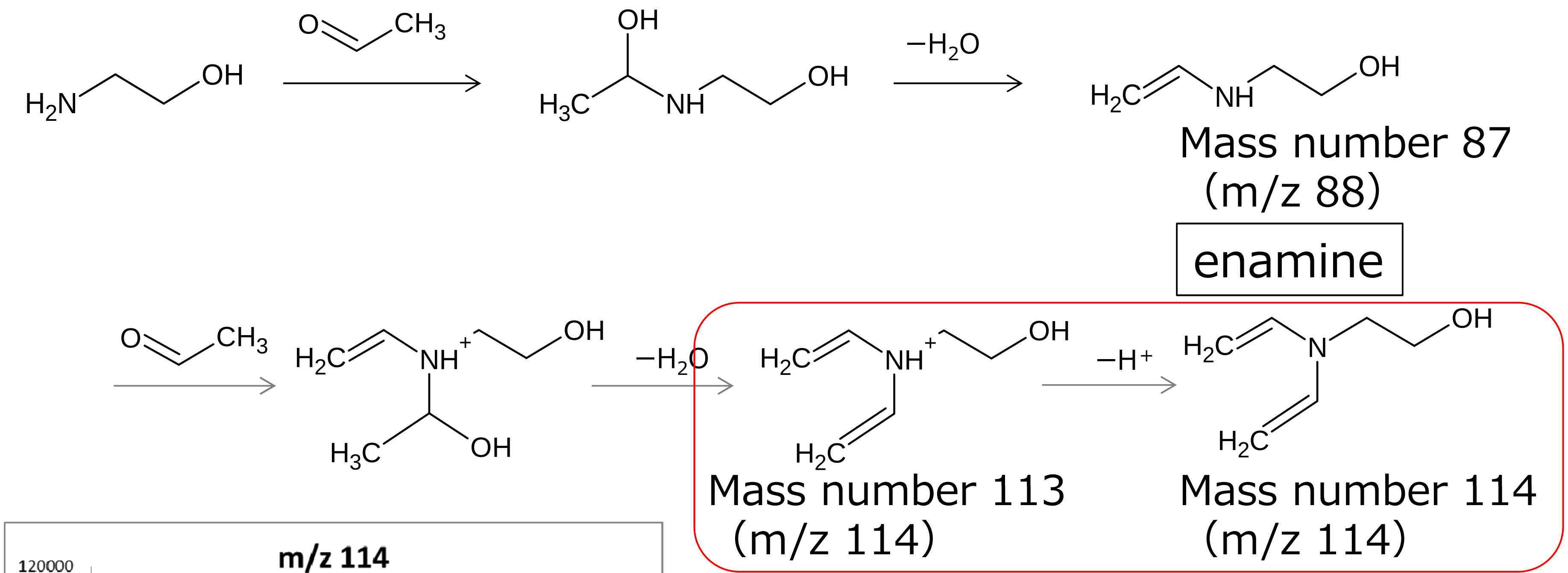
Under basic condition



Mass number 87
(m/z 88)

enamine

Reaction mechanisms of MEA and two acetaldehydes



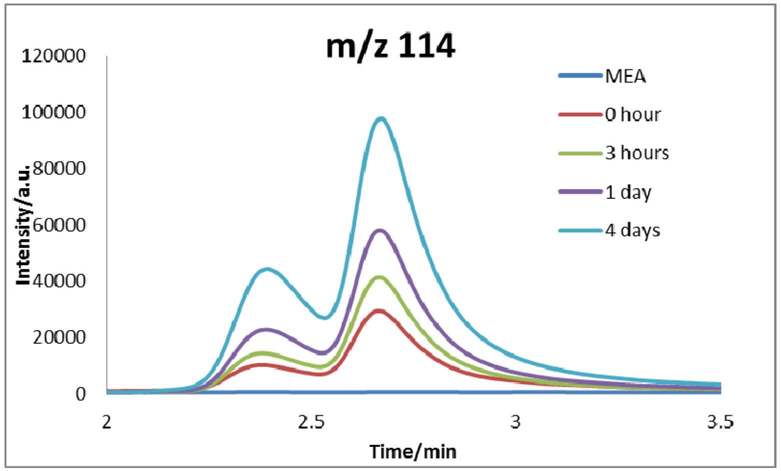
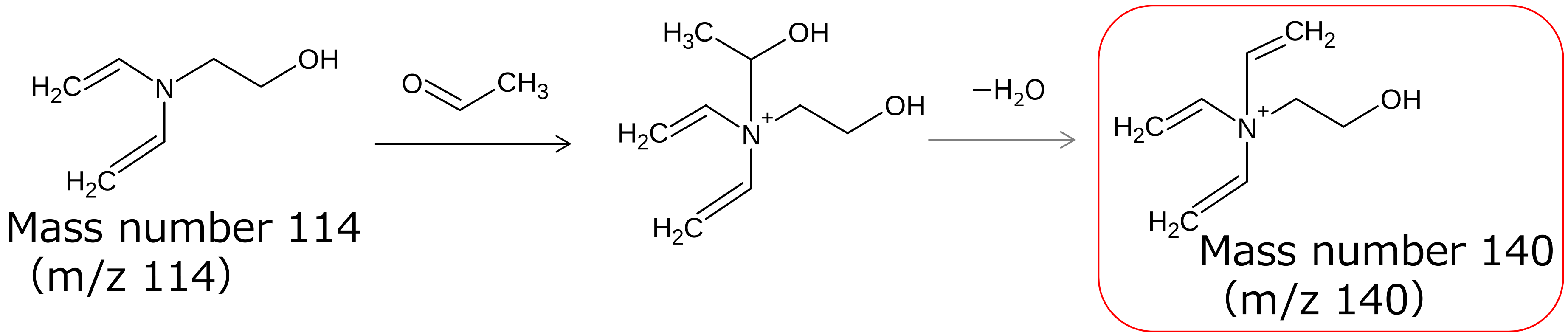


Fig. m/z 114 Chromatogram of LC/MS

Enamines can react with another aldehyde.
The m/z 114 compound is the dienamine that MEA combined with two acetaldehydes.

Reaction mechanisms of MEA and three acetaldehydes

If another acetaldehyde reacts with MEA combined with two acetaldehydes, the m/z 140 compound is formed.



When the addition amount of aldehyde is large, quaternary ammonium（m/z 140 ;in the case of MEA） is formed.

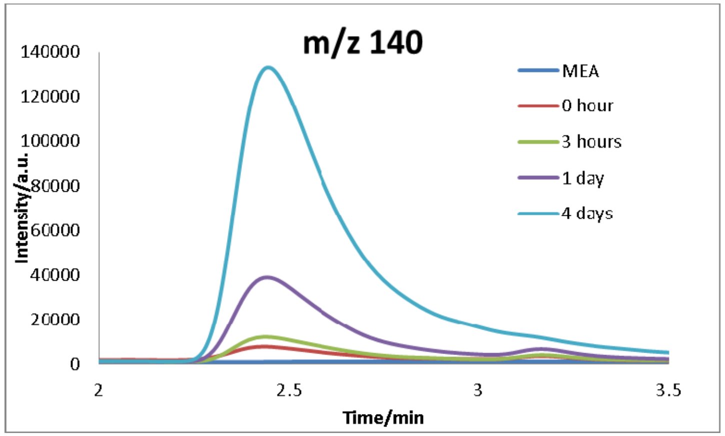


Fig. m/z 140 Chromatogram of LC/MS

Recovery amount of aldehydes in MEA aqueous solution

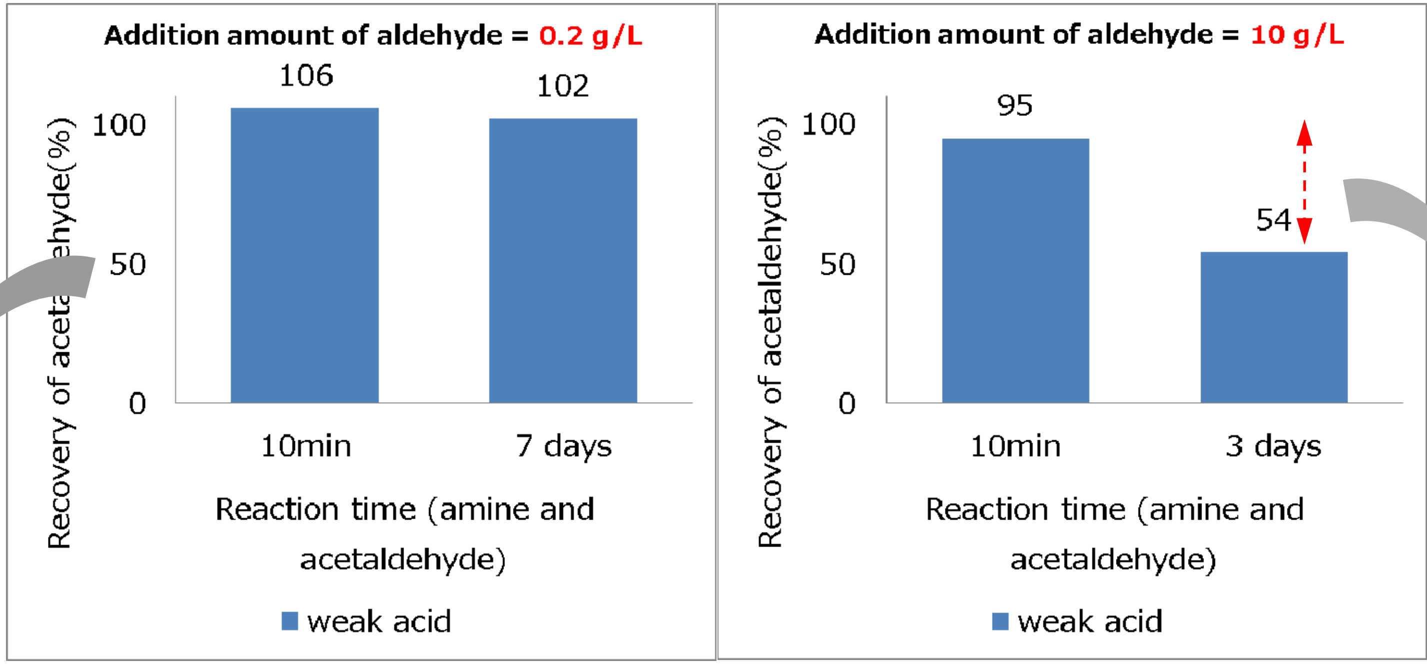


Fig. Recovery amount of aldehyde in MEA

Addition amount of aldehyde is small

enamine
(Secondary or tertiary amine)

<ins>Reversible reaction</ins>

Addition amount of aldehyde is large

Quaternary ammonium

<ins>Irreversible reaction</ins>

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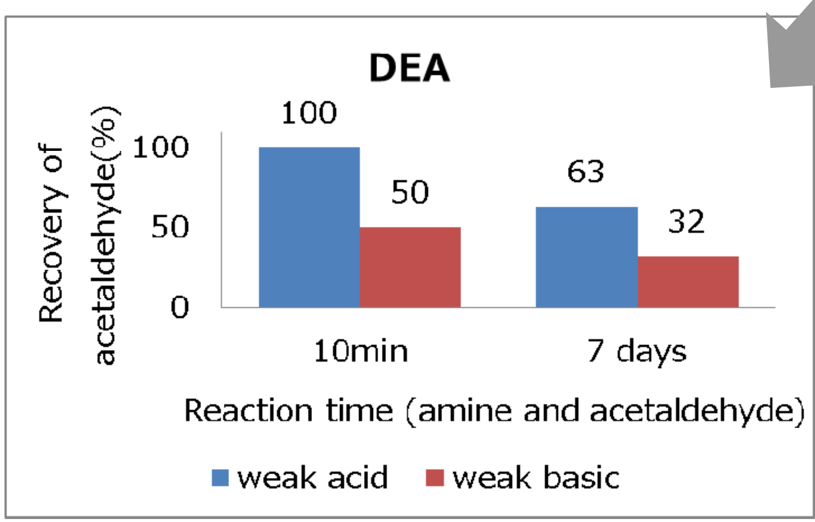
Recovery amount of aldehyde in DEA aqueous solution

Table Recovery amount of aldehyde in DEA

Sample	Addition amount of aldehyde	Reaction time (amine and aldehyde)	Derivatization pH	Recovery of acetaldehyde (%)
Water	0.2g/L	-		100
DEA (50g/L)	0.2g/L	10 min	Weak-acid	100
		10 min	Weak-basic	50
		7 days	Weak-acid	63
		7 days	Weak-basic	32



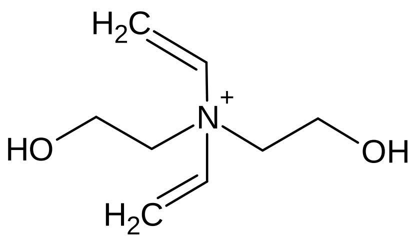
When the reaction time was long, the recovery amount of aldehyde was low in the case of DEA.

Fig. Recovery amount of aldehyde in DEA

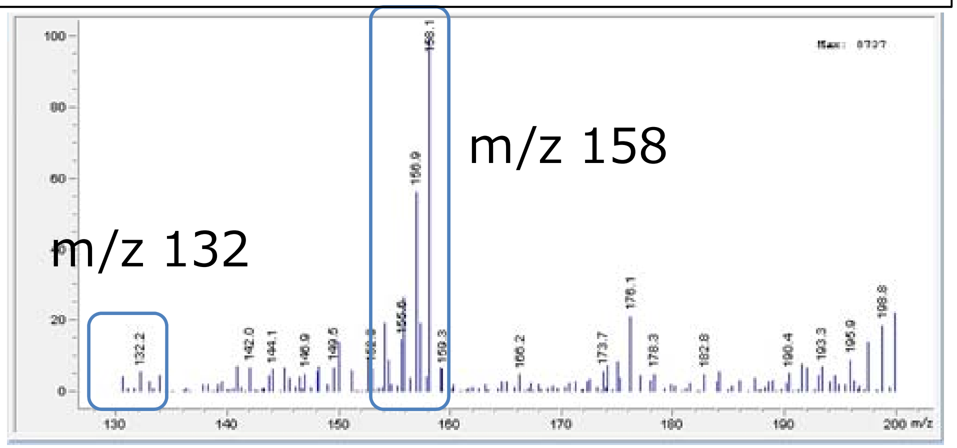
LC/MS analysis of DEA reacted with acetaldehyde

Three days after addition of acetaldehyde

Quaternary ammonium from DEA:m/z 158

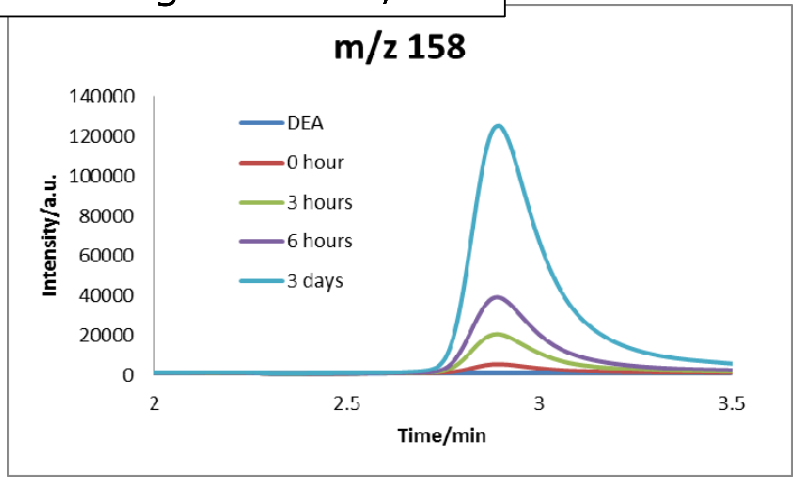


Mass spectrum of DEA containing acetaldehyde.



The quaternary ammonium ion (m/z 158) were detected. The tertiary amine (m/z 132) was also detected, but the amount was smaller than m/z 158.

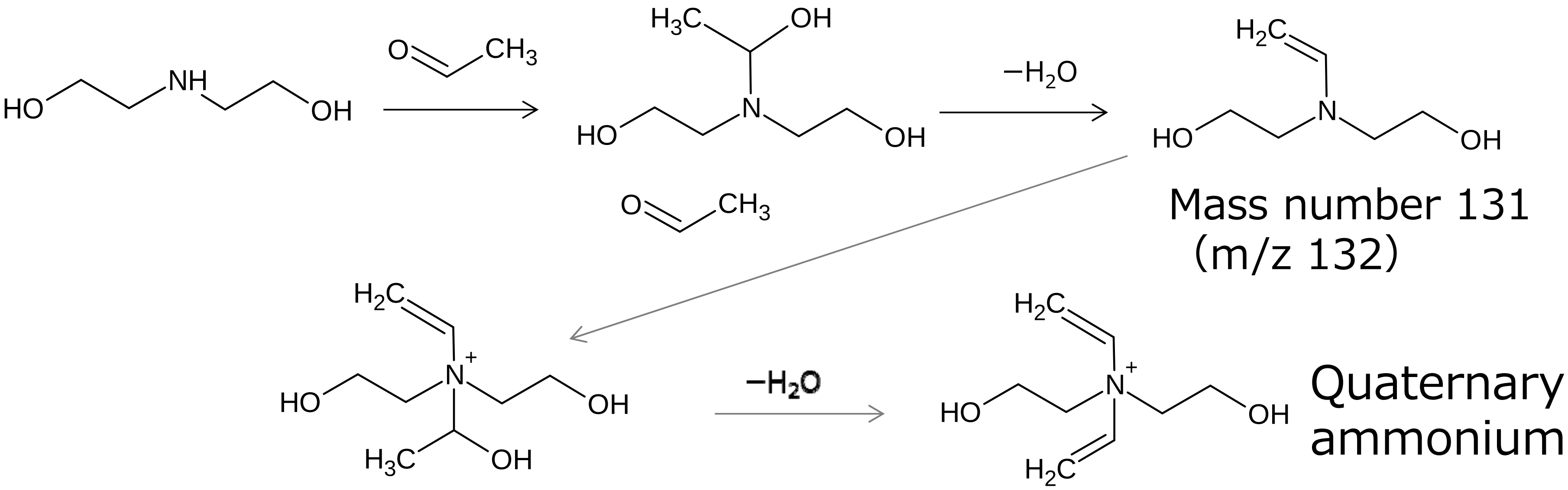
Chromatogram of LC/MS



Recovery amount of aldehyde in DEA aqueous solution

Table Recovery amount of aldehyde in DEA

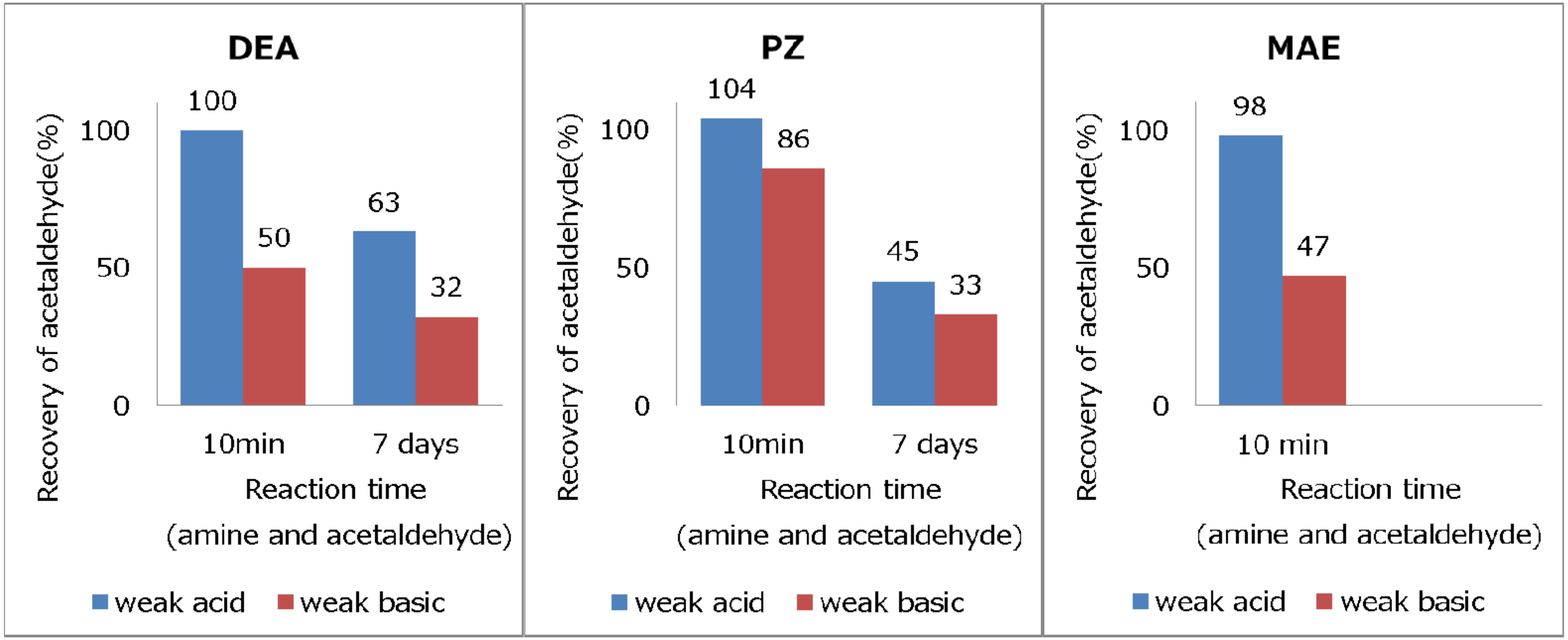
Sample	Addition amount of aldehyde	Reaction time (amine and aldehyde)	Derivatization pH	Recovery of acetaldehyde (%)
DEA (50g/L)	0.2g/L	7 days	Weak-acid	63
		7 days	Weak-basic	32



Mass number 158 (m/z 158)

Since the quaternary ammonium was preferably formed, the recovery amount of aldehyde was low.

Aldehyde recovery in secondary amine aqueous solution



amine amount 50g/L, Addition amount of aldehyde 0.2g/L

Fig. Recovery amount of aldehyde in secondary amines

The recovery amount of aldehyde was low in the case of the other secondary amines.

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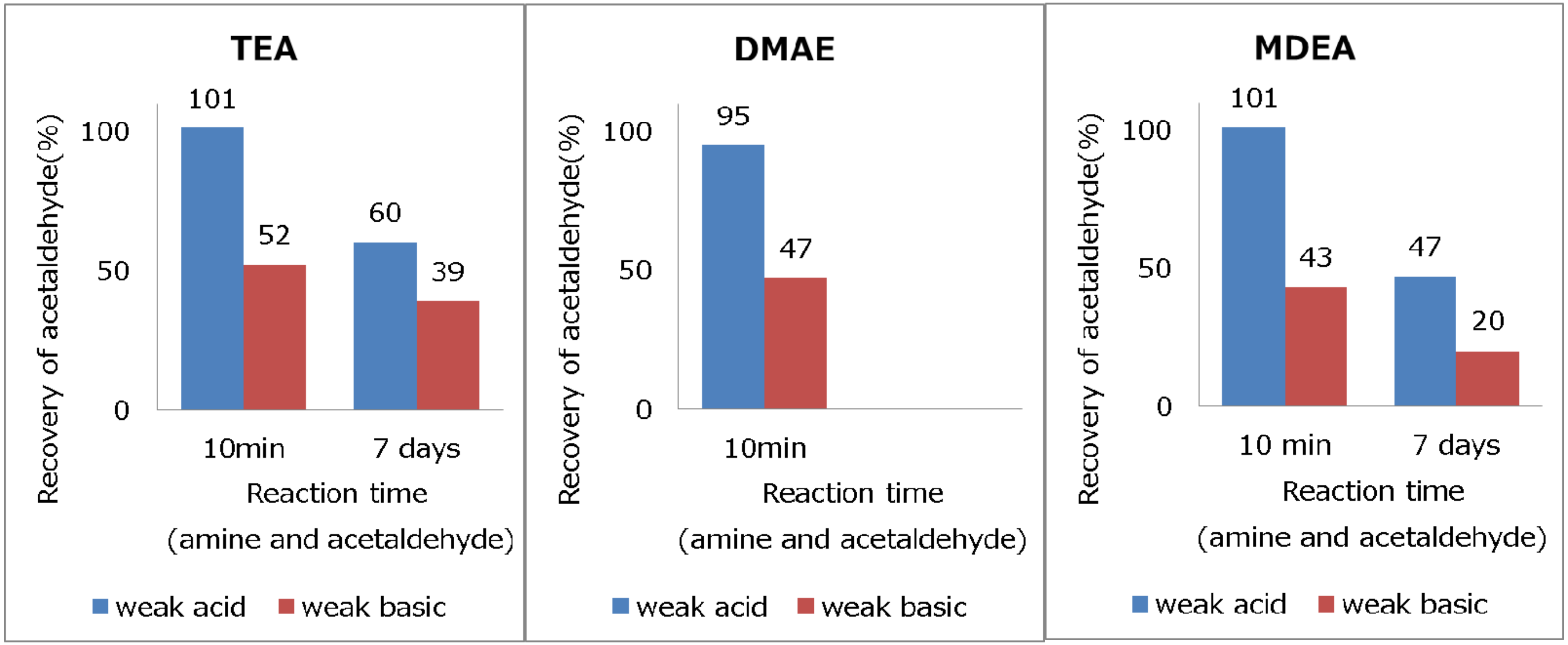
Aldehyde recovery in tertiary amine aqueous solution



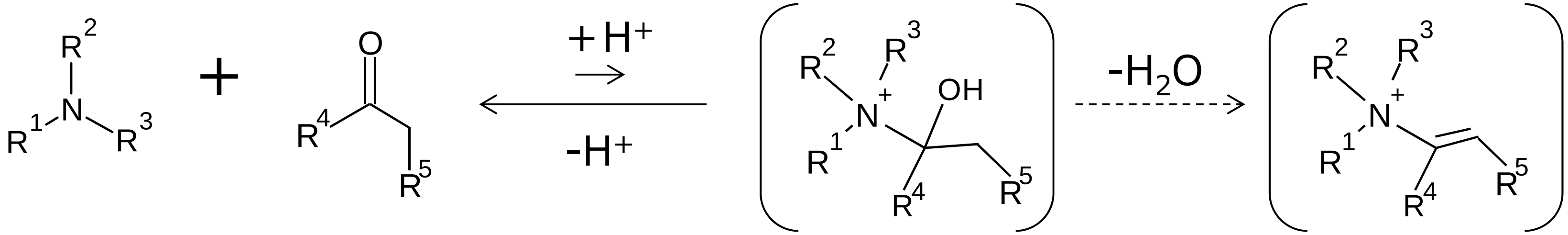
amine amount 50g/L, Addition amount of aldehyde 0.2g/L

Fig Recovery amount of aldehyde in tertiary amines

The recovery amount of aldehyde was also low in the case of tertiary amines.

Reaction mechanisms of tertiary amine and acetaldehyde

Since tertiary amines reacted with aldehyde are unstable, the reverse reaction is considered superior.



m/z 164

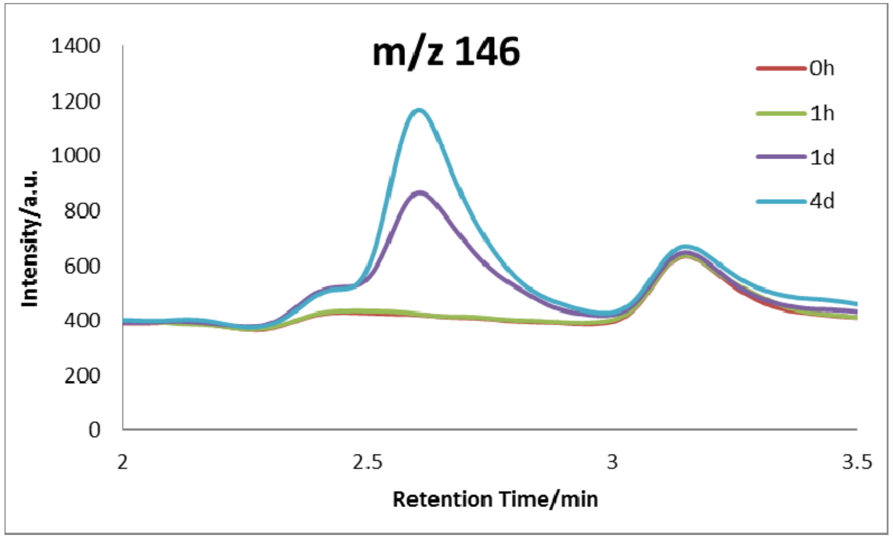
Though Aldehyde recovery was low.
→ Investigation of MDEA reaction products

LC/MS analysis of MDEA

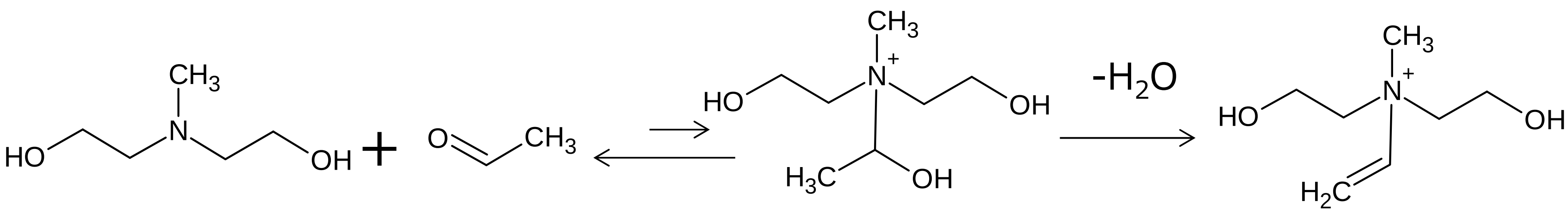
After addition of acetaldehyde, m/z 146 increased.

m/z 146
＝quaternary ammonium from MDEA

Chromatogram of LC/MS

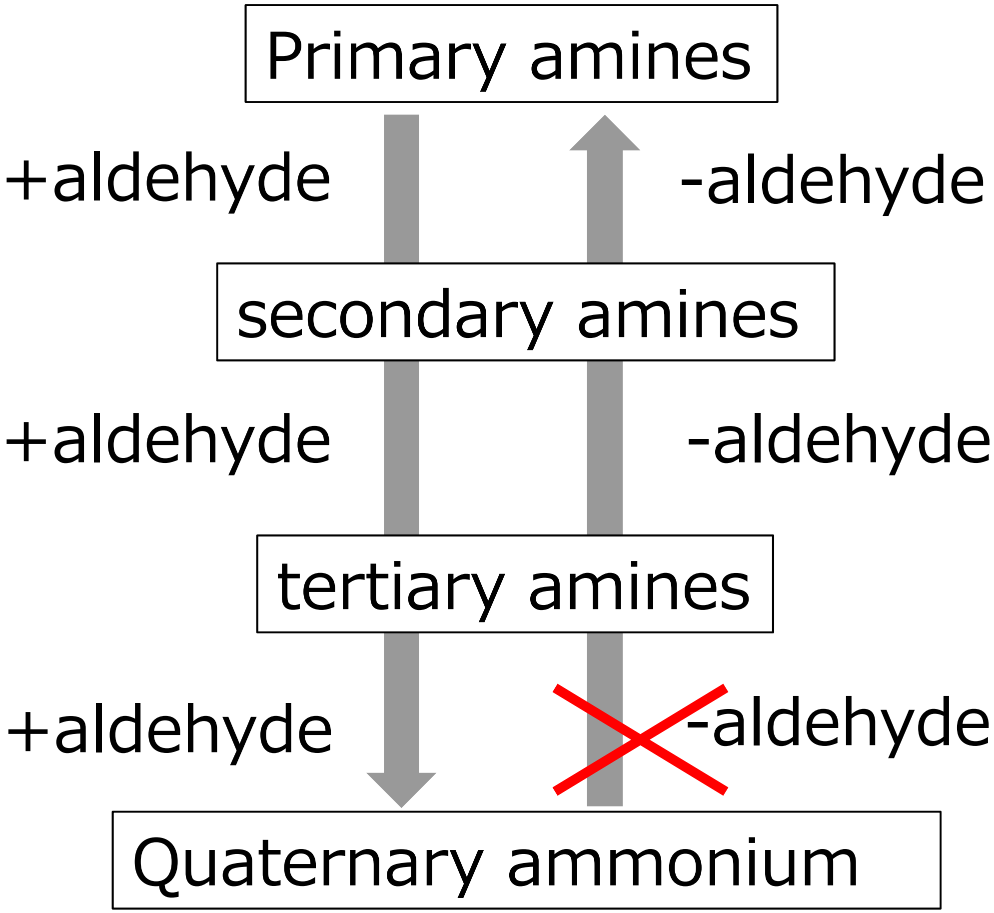


→ Even tertiary amines might react with acetaldehydes and quaternary ammonium might be formed.



m/z 146

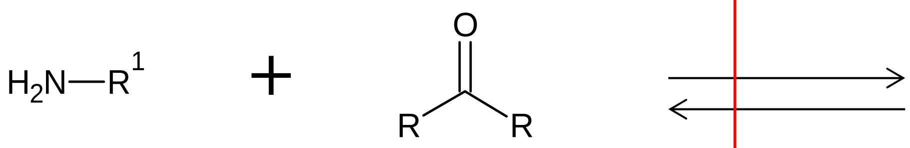
Amines reacted with aldehydes



Formation of quaternary ammonium is irreversible reaction.

For stable analysis of aldehyde in amine aqueous solution

Since amine absorbent pH is basic, aldehyde reaction with amine proceed, and form imine and enamine.



Imines, enamines···

Aldehydes

Low pH
(weak acidic condition)

High pH
(basic condition)

Analysis of aldehyde amount in absorbent
・Stored in acid condition
・Quick analysis(before reaction progress)

Summary

◆In this study, the uncommon reactions between acetaldehyde and amine absorbents were described.

・Amine solution containing acetaldehyde results in enamines and imines.

・All amines, which are primary, secondary, or tertiary, could form quaternary ammonium with acetaldehyde.

◆Quantitative analysis of aldehydes in amine absorbent requires care because aldehydes react with amines.

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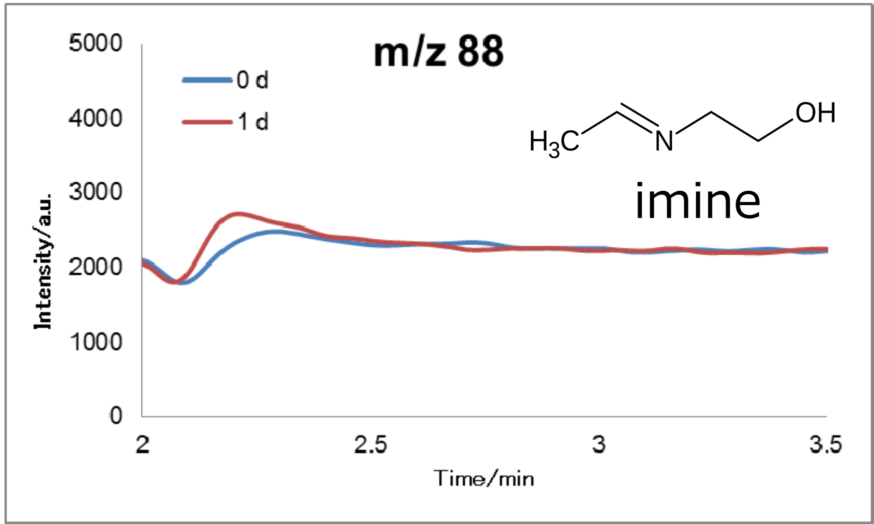
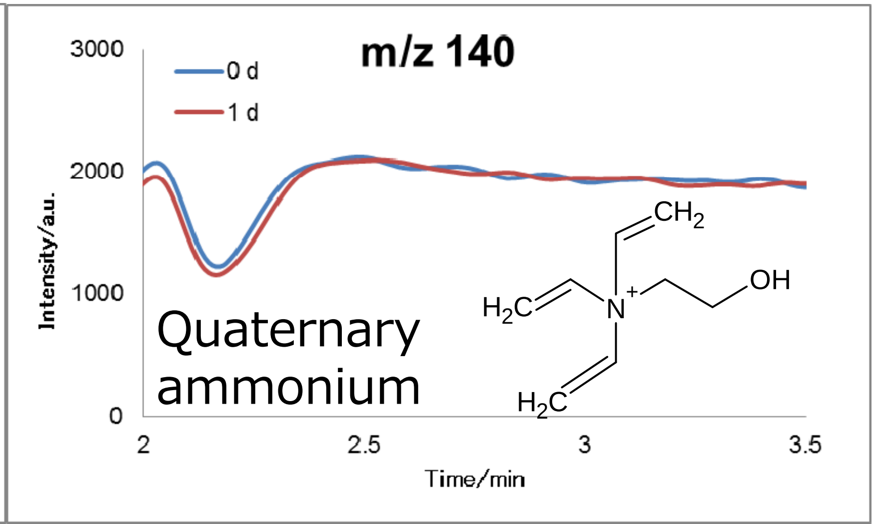
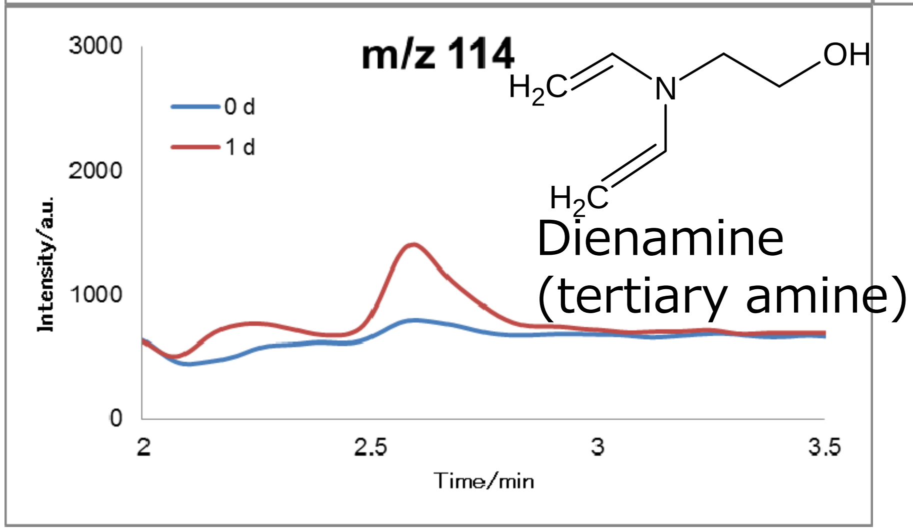
LC/MS analysis of MEA reacted with acetaldehyde (1g/L)







When addition amount of aldehyde was 1g/L, MEA formed imine and dienamine but quaternary ammonium in one day.

TOSHIBA Carbon Capture plant

TOSHIBA Corporation engages in CCS/CCU technology deployment.

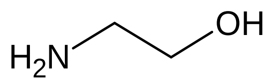
CCU demonstration plant in
SAGA, JAPAN（10～20kg/d-CO_2）

CCS demonstration plant in
FUKUOKA, JAPAN（10 t/d-CO_2）

*Photo from TOSHIBA website
http://www.toshiba.co.jp/thermalhydro/en/thermal/products/ccs/ccs.htm

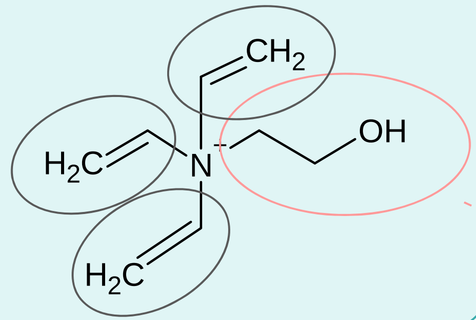
What will be formed from quaternary ammonium ion?

for example; MEA



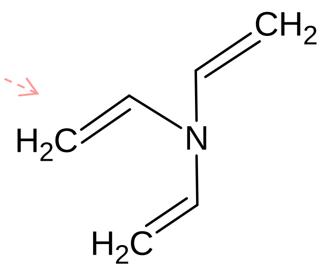
+ three acetaldehydes

Quaternary ammonium ion



2-hydroxy-ethyl

To other compounds

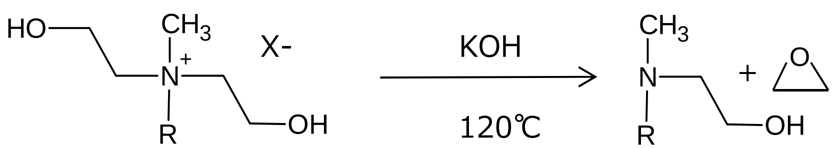


Double bond
・Polymerization?
→foaming?
・Oxidation?

Substituent group
・transferring

Reference

Y. Hayashi, *J. Jpn. Oil. Chem. Soc.* ,**Vol.36, No.6**, 409(1987)



The Ethanol group is selectively eliminated from dihydroxyethyl ammonium salt under basic condition.

There is possibility that quaternary ammonium from amines and aldehydes forms many deteriorating products.

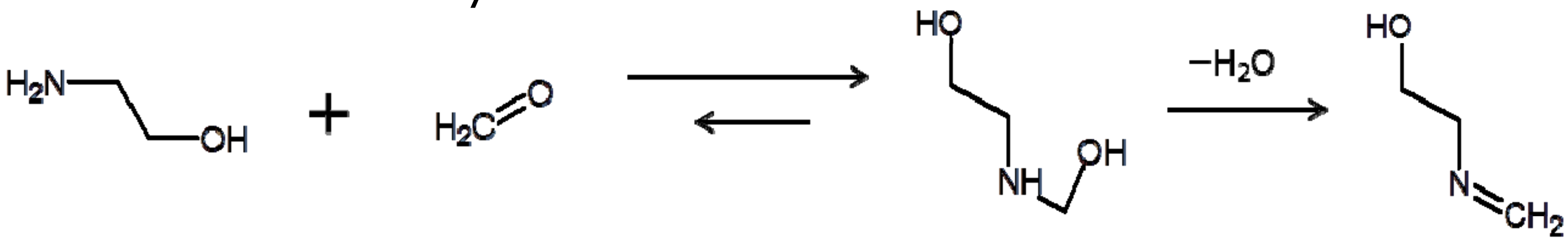
Formaldehyde reaction with amine

Sample	Addition amount of aldehyde	Reaction time (amine and aldehyde)	Derivatization pH	Recovery of acetaldehyde (%)
Water	0.2g/L	-		100
MEA (50g/L)	0.2g/L	10 min	Weak-acid	95
		10 min	Weak-basic	98
		4 days	Weak-acid	97
		4 days	Weak-basic	101
DEA (50g/L)		10 min	Weak-acid	94
		10 min	Weak-basic	101
		4 days	Weak-acid	105
		4 days	Weak-basic	105

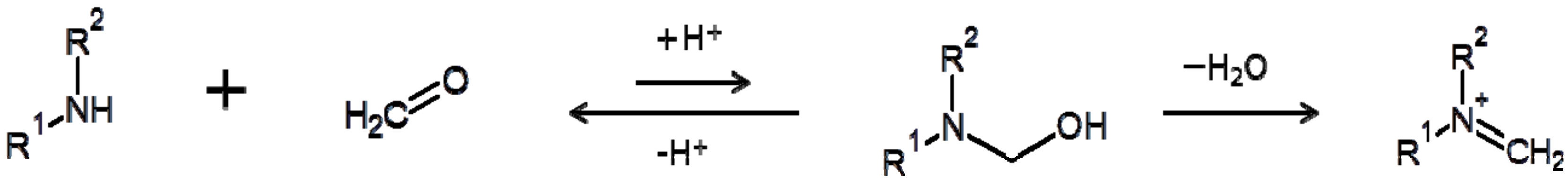
Recovery amount of formaldehyde is 100% in any cases

Reaction mechanisms of amine and formaldehyde

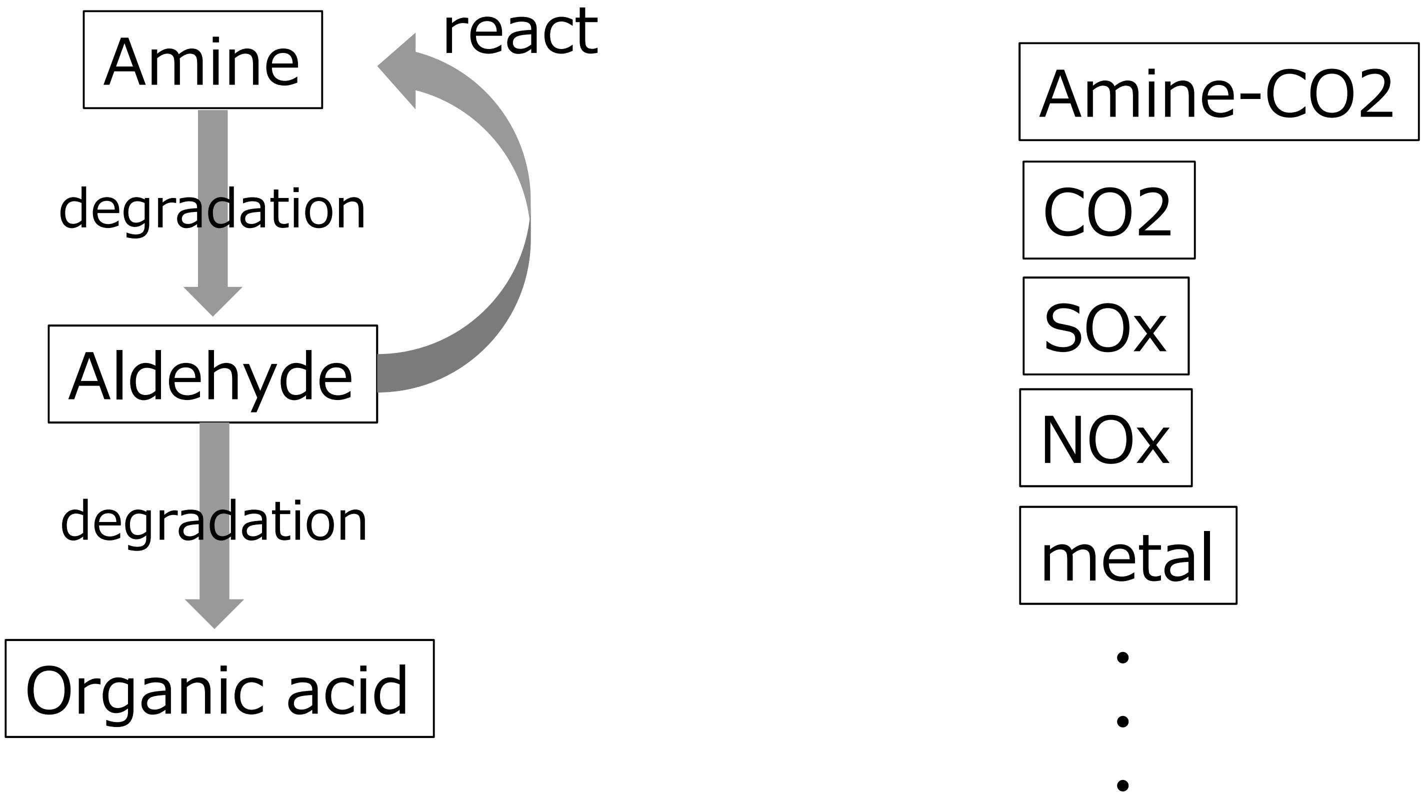
MEA and formaldehyde



Secondary amine and formaldehyde



Reversible reaction


Amine
react
degradation
Aldehyde
degradation
Organic acid
Amine-CO2
CO2
SOx
NOx
metal

Aldehyde recovery in secondary amine aqueous solution

Table Recovery amount of aldehyde in secondary amines

Sample	Addition amount of aldehyde	Reaction time (amine and aldehyde)	Derivatization pH	Recovery of acetaldehyde (%)
Water	0.2g/L	-		100
DEA (50g/L)	0.2g/L	10 min	Weak-acid	100
		10 min	Weak-basic	50
		7 days	Weak-acid	63
		7 days	Weak-basic	32
PZ (50g/L)		10 min	Weak-acid	104
		10 min	Weak-basic	86
		7 days	Weak-acid	45
		7 days	Weak-basic	33
MAE (50g/L)		10 min	Weak-acid	98
		10 min	Weak-basic	47

Aldehyde recovery in tertiary amine aqueous solution

Table Recovery amount of aldehyde in tertiary amines

Sample	Addition amount of aldehyde	Reaction time (amine and aldehyde)	Derivatization pH	Recovery of acetaldehyde（%）
Water	0.2g/L	-		100
TEA (50g/L)	0.2g/L	10 min	Weak-acid	101
		10 min	Weak-basic	52
		7 days	Weak-acid	60
		7 days	Weak-basic	39
DMAE (50g/L)		10 min	Weak-acid	95
		10 min	Weak-basic	47
MDEA (50g/L)		10 min	Weak-acid	101
		10 min	Weak-basic	43
		7 days	Weak-acid	47
		7 days	Weak-basic	20