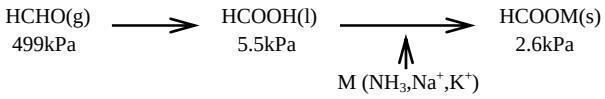
Study on generation mechanism of formic acid in indoor environments
(室内環境中のギ酸生成メカニズムの解明)

4ASCM011　Keisuke MIYASHIRO
Supervisor　Dr. Yoshika SEKINE

1.Introduction

In modern living environments, human can be exposed to numerous types of pollutants in indoor air. However, secondary emission products generated through chemical reactions have not been fully concerned in relation to so-called Sick Building/House Syndrome. We focused on secondary formation of formic acid (HCOOH) suspected to have any impacts on human health such as chemical sensitivity. The important precursor of HCOOH could be formaldehyde (HCHO) in Japanese modern houses. When a formate was subsequently formed by a reaction with basic substances (eg. NH_3), particulate formate species could be found in the air due to lower vapor pressures. Then, authors have developed separative sampling method of gaseous and particulate HCOOH in indoor air, and the formation mechanism was investigated by a small chamber and field experiments. In this study, as formate species were not identified, concentration of formate/formic acid was shown as HCOOH.



2.Experimental

2.1 Development of separative sampling of formate / formic acid

Sampling device consists of miniature diffusion scrubber (MDS, Gastec), impinger and air suction pump, serially connected by silicone tube. Trapping solution was KOH(aq) for formate / formic acid. Collection efficiencies and back trapping of the MDS was examined by varying KOH concentration and flow rate, and then validated.

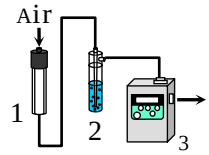


Fig.1 Separative sampling device of formate species.

1:MDS (7mM-KOH,1ml)
2:Impinger (1mM-KOH, 5ml)
3:Pump

2.2 Examination of HCOOH generation mechanism

Generation mechanism of formate / formic acid was investigated using a small chamber with a constant gas intrduction system.

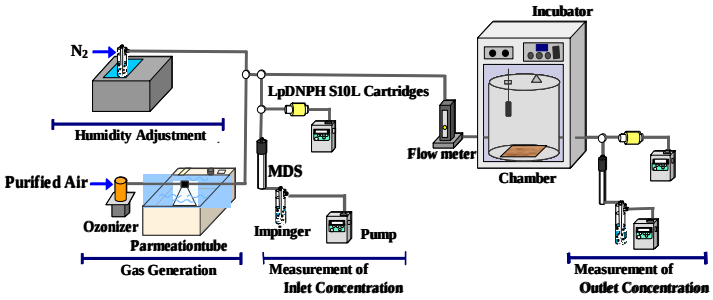


Fig.2 Layout of chamber experiment

<Experimental condition>

Carrier gas:N_2,Purified air

Air exchange rate:1(/h)

Loading factor : 2.25 (m^2/m^3)

HCHO emission rate : 40.8(μg/m^2/h)

Chamber volume:20 (L)　Temperature : 25 (℃)　Relative humidity : 50 (%)

O_3 concentration : 0 ~ 1000 (μg/m^3)　NO_2 concentration : 0 ~1000(μg/m^3)

2.3 Field measurement

Field measurements was conducted in a teaching room of Tokai university and apartment house. The change in the form of formate / formic acid with time was also monitored.

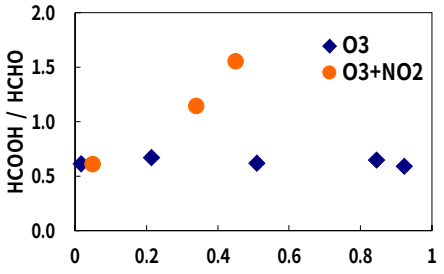
3.Result and Discussion

3.1 Separative sampling of HCOOH

Collection efficiency of gaseous HCOOH by MDS resulted in 94% under the following condition : 0.1 L/min of flow rate and 1ml of 7mM-KOH as trapping solution. The total amount of HCOOH collected by the separative sampling equaled to that by previous overall sampling using impinger only.

3.2Examination of HCOOH generation mechanism

When only O_3 was injected in the chamber, HCOOH/HCHO concentration ratio emitted from plywood was almost constant. On the other hand, when O_3 and NO_2 were injected in the chamber, HCOOH/HCHO concentration ratio plywood was increased(Fig.3). O_3 and NO_2 were necessary for the generation of HCOOH. This suggests nitrate radical(NO_3), which can be formed by the reaction of O_3 and NO_2, plays a important role of generation of HCOOH. Formation of particulate HCOOH increased when the ammonia gas was injected in the chamber. This means particulate formate species generates with a reaction of the basic material such as ammonia in air with HCOOH(Fig.4).



L:2.25(m²/m³) T:25(℃) R.H.:50(%)
Fig.3 Influence of Ox concentration on HCOOH generation

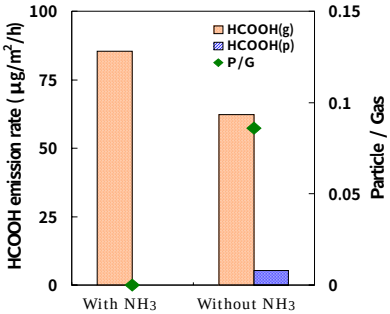


Fig.4 Influence of NH3(g) on the formation of HCOOH(p)

3.3 Field measurement

While both gaseous and particulate form of HCOOH were detected in indoor air, Concentration of particulate form detected before ventilation in the apartment house. Concentration of particulate form decreased after ventilation(Fig.5). This suggests HCOOH firstly generates as gaseous form and then changes to aerosol particles, probably with a reaction of basic substances. Therefore, We investigated time course of forms of HCOOH in indoor air.After air exchanging, gaseous form firstly generated and then, gradually changed to particulate form(Fig.6).

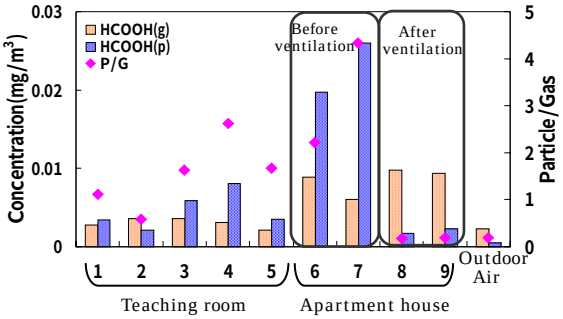


Fig.5 Resolute of field measurement

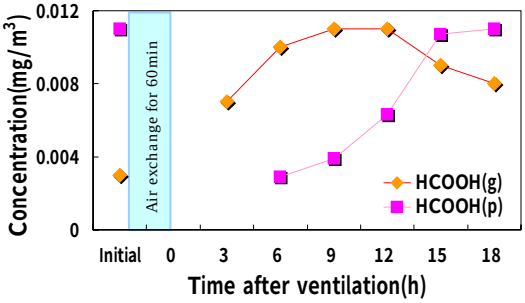


Fig.6 Time course of forms of HCOOH

4.Conclusion

This study showed that HCOOH generates in indoor environments by reaction of HCHO and NO_3 radical, and form gradually changes from gas to particle by coupling with basic substances.