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Formaldehyde vapor produced from hexamethylenetetramine and pesticide: Simultaneous monitoring of formaldehyde and ozone in chamber experiments by flow-based hybrid micro-gas analyzer

Akira Yanaga^a, Naruto Hozumi^a, Shin-Ichi Ohira^a, Asako Hasegawa^b, Kei Toda^{a,*}^a Department of Chemistry, Kumamoto University, Kumamoto 860-8555, Japan^b Department of Architecture and Building Engineering, Kumamoto University, Kumamoto 860-8555, Japan

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ABSTRACT

Simultaneous analysis of HCHO and O₃ was performed by the developed flow analysis system to prove that HCHO vapor is produced from solid pesticide in the presence of O₃. HCHO is produced in many ways, including as primary emissions from fuel combustion and in secondary production from anthropogenic and biogenic volatile organic compounds by photochemical reactions. In this work, HCHO production from pesticides was investigated for the first time. Commonly pesticide contains surfactant such as hexamethylenetetramine (HMT), which is a heterocyclic compound formed from six molecules of HCHO and four molecules of NH₃. HMT can react with gaseous oxidants such as ozone (O₃) to produce HCHO. In the present study, a flow analysis system was developed for simultaneous analysis of HCHO and O₃, and this system was used to determine if solid pesticides produced HCHO vapor in the presence of O₃. HMT or the pesticide jimandaisen, which contains mancozeb as the active ingredient and HMT as a stabilizer was placed at the bottom of a 20-L stainless steel chamber. Air in the chamber was monitored using the developed flow system. Analyte gases were collected into an absorbing solution by a honeycomb-patterned microchannel scrubber that was previously developed for a micro gas analysis system (μ GAS). Subsequently, indigotrisulfonate, a blue dye, was added to the absorbing solution to detect O₃, which discolored the solution. HCHO was detected after mixing with the Hantzsch reaction reagent. Both gases could be detected at concentrations ranging from parts per billion by volume (ppbv) to 1000 ppbv with good linearity. Both HMT and jimandaisen emitted large amount of HCHO in the presence of O₃.

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1. Introduction

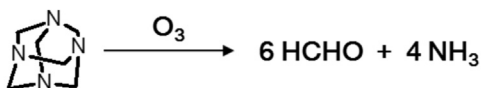
In this work, an analytical system for simultaneous measurement of formaldehyde (HCHO) and ozone (O₃) was developed to investigate production of HCHO vapor from the reaction of pesticide with O₃. HCHO is a harmful and toxic volatile compound [1] that is ubiquitous in both indoor and outdoor air. Gaseous HCHO is primary emitted from the combustion of fossil fuels [2], biomasses [3] and tobacco smoke [4]. Additionally, secondary production of HCHO from the reactions of several biogenic volatile compounds (e.g. isoprene, terpenes) with oxidants [5–8]. In forest air, HCHO production rates varied diurnally because of changes in biogenic volatile organic compounds and oxidant concentrations [9]. The produced gaseous HCHO enters PM_{2.5}, such as ammonium sulfate aerosols, during aerosol growth [10]. In addition to the secondary production routes in the gas phase, HCHO can be produced from

solid pesticides in heterogeneous reaction with oxidants, but not by the homogeneous gaseous reactions.

One such pesticide that is able to produce HCHO is jimandaisen (Fig. 1), which contains mancozeb ([C₄H₆N₂S₄Mn]_x[Zn]_y) as its active ingredient (70%). Jimandaisen is commonly sprayed on leaves (Fig. 1) to control purple blotch disease. However, the pesticide does not adhere to the leaves very well and can be washed off by rain. Therefore, like in many other pesticides, a surfactant is added to jimandaisen for stabilization. The surfactant hexamethylenetetramine (HMT, C₆H₁₂N₄, MW 140.19) is present at a mass fraction of 3% in this pesticide. The HMT is a heterocyclic compound formed from six molecules of HCHO and four molecules of NH₃. HMT vaporization is minimal because of its low vapor pressure (0.53 Pa (4.0 × 10⁻³ Torr) at 25 °C) [11] and high water solubility (Henry's law constant: 6.1 × 10⁵ mol L⁻¹ atm⁻¹) [12]. Additionally, HMT is weakly protonated to HMTH⁺ at low pH (pK_a of HMTH⁺ = 4.89) [13]. Accordingly it emitted to the atmosphere as HMT vapor. However, in the presence of O₃, HMT may produce gaseous HCHO emissions. In Japan, aqueous HMT was involved in the contamination of the Tone river with HCHO in May

* Corresponding author.

E-mail address: todakei@sci.kumamoto-u.ac.jp (K. Toda).



Hexamethylenetetramine (HMT)

Fig. 1. Images of pesticide packaging and the pesticide sprayed on leaves. The equation shows decomposition of HMT to HCHO and NH_3 .

2012 [14]. In this case, HMT, which was produced by mixing HCHO and NH_3 in industrial wastewater, decomposed to HCHO during chlorine treatment of drinking water. This incident shows that HMT can be decomposed by an oxidant and acid to HCHO and NH_3 in water. It also suggests that solid HMT sprayed in agricultural applications may emit HCHO on reaction with oxidants such as gaseous O_3 , which is ubiquitous and present at concentrations of up to 100 parts per billion by volume (ppbv) on sunny days. We previously developed a wastewater monitor that could analyze for total HCHO and HMT concentrations every 15 min [15,16]. This method was based on the decomposition of HMT to HCHO vapor. To date, HCHO production from pesticides has not been investigated. The aim of this research was to develop a method for simultaneously monitoring HCHO and O_3 . To detect HCHO and O_3 , we applied the Hantzsch reaction [17,18] and indigotrisulfonate (ITS) discoloration [19,20], respectively (Fig. 2). The ozone decomposition of ITS results in a disruption of its π -electron conjugated system and the elimination of the system's absorption in the red region. The analytical system used was based on the micro gas analysis system (μGAS) [21–23]. Analyte gas molecules were collected in a honeycomb-patterned microchannel scrubber, which can concentrate gases up to 20,000-fold more than a conventional gas bubbling impinger [21]. Recently we developed a μGAS for atmospheric HCHO [9] and CH_3SH near the odor detection threshold level [24]. In this work, simultaneous gas analysis was examined using a μGAS technique with a single scrubber for the

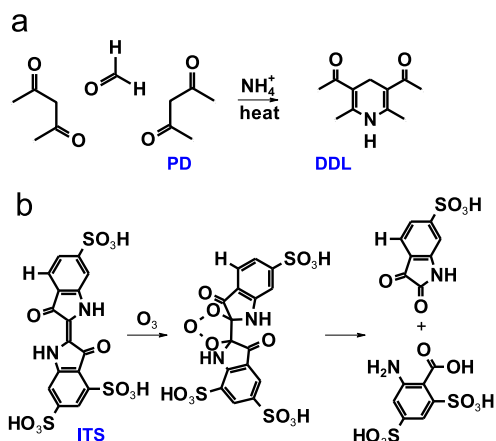


Fig. 2. Hantzsch reaction (a) and decomposition of indigotrisulfonate (ITS) and (b) for measuring HCHO and O_3 , respectively.

first time, and the two gases were monitored in chamber experiments to determine if HCHO was produced from HMT and Jimandaisen.

2. Experimental

2.1. Reagents

The absorbing solution flowing through the microchannel scrubber was $10 \mu\text{mol L}^{-1}$ ITS in 10 mmol L^{-1} H_2SO_4 . ITS was obtained from Tokyo Kasei, Tokyo, Japan. The Hantzsch reaction reagent solution, which was mixed with the absorbing solution after gas absorption, was a mixture of 0.01 mol L^{-1} 2,4-pentanedione (PD) (Tokyo Kasei), $0.25 \mu\text{mol L}^{-1}$ acetic acid (Nacalai Tesque, Kyoto, Japan) and $2 \mu\text{mol L}^{-1}$ ammonium acetate (Nacalai Tesque). Stock solutions for the reagent solution were prepared at concentrations three times higher than those in the working solution and were mixed in a 1:1:1 volume ratio just before use.

Standard HCHO gas (10 ppbv) was prepared by bubbling purified air (0.2 L min^{-1}) through $82 \mu\text{mol L}^{-1}$ aqueous HCHO (20°C) and immediate dilution with dry air (0.2 L min^{-1}) to prevent water saturation. Ozone contained in laboratory room air was used as it was. Alternatively, O_3 generated by a UV-lamp was introduced at 0.4 L min^{-1} for 1 or 3 min to give a chamber O_3 concentrations of approximately 200 or 800 ppbv, respectively. Calibration of ITS O_3 monitoring was performed by connecting a commercial O_3 monitor (Model 49i, Thermo Fisher Scientific, Waltham, MA, USA) to the O_3 test gas line. The commercial O_3 monitor was used only for calibration and not for monitoring the chamber air because its air sampling rate (1.8 L min^{-1}) was too high for the chamber volume.

HMT was purchased from Nacalai Tesque, and Jimandaisen was obtained from Dow Chemical Japan, Tokyo.

2.2. Measurement system

Fig. 3 shows the analytical system used for the chamber experiments. Red lines are the gas sampling lines including the chamber experiment, and blue lines represent liquid flow for gas absorption and detection of the absorbed species. Control of gas sampling was performed by a pair of three-way solenoid valves (MTV-3-1/4UFH-3, Takasago Electric, Nagoya, Japan) as shown in Fig. 3. Normally, ambient air was introduced to the microchannel scrubber at a flow rate of 0.2 L min^{-1} , via a purification column packed with activated carbon. The pump outlet air was sent to waste to obtain a baseline signal using the purified ambient air. When the three-way solenoid valves were switched on, the chamber air was introduced to the scrubber, and waste gas was taken back to the chamber to maintain the chamber pressure constant without air exchange. The microchannel scrubber was comprising of polydimethylsiloxane channel plate covered with a porous polytetrafluoroethylene sheet (Pereflon HP-045-30, thickness $30 \mu\text{m}$, pore size $0.45 \mu\text{m}$), and is described in detail elsewhere [21,22]. The absorbing and reagent solutions were pumped at $150 \mu\text{L min}^{-1}$ each using a peristaltic pump (Minipuls, Gilson, Middleton, WI) equipped with $0.5 \text{ mm i.d.} \times 3.7 \text{ mm o.d.}$ Pharmed[®] tubing. The absorbing solution from the scrubber was introduced to a flow-through absorbance detector (UV-1570, Jasco, Tokyo, Japan) to monitor decrease in ITS concentration at 600 nm . Then, the absorbing solution was mixed with the Hantzsch reaction reagent solution, and the collected HCHO was reacted with PD in the reaction coil ($0.5 \text{ mm i.d.} \times 1/16'' \text{ o.d.} \times 1500 \text{ mm l}$) rounded on a porcelain resistor (47Ω) powered by DC 12 V. The temperature of the coil was maintained at 65°C by a thermocontroller (E5CN-RTC, Omron, Kyoto, Japan). Generation of the product, 3,5-

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