

Decomposition of volatile organic carbon with photo-oxidation

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Abstract:

The oxidation behavior of ethylene and methanethiol were investigated in the systems of ultraviolet (UV) light/hydrogen peroxide aqueous solution and UV/hydrogen peroxide aqueous solution/wire mesh to evaluate the usefulness of UV irradiation for the oxidation of volatile organic compounds. The light induced chemical absorption of ethylene was observed. UV irradiation induced the chemical absorption of ethylene; ethylene was not oxidized directly by UV irradiation, and it did not dissolve into hydrogen peroxide aqueous solution in the absence of UV irradiation. Ethylene was converted to intermediates that dissolve in the liquid phase. Carbon dioxide evolved drastically after the disappearance of ethylene in the gas phase. The methanethiol concentration decreased drastically by UV irradiation in the UV/hydrogen peroxide system while the intermediates produced by the direct photodecomposition tended to remain in the gas phase. The UV/hydrogen peroxide/wire mesh system accelerated the oxidation of the intermediates in liquid phase as well as the intermediates in the gas phase according to the photo-Fenton reaction.

Keywords: Ethylene; Hydrogen peroxide; Light induced chemical absorption; Methanethiol; UV; VOCs

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1. Introduction

In order to develop an efficient process for removing and oxidizing VOCs, we investigated an ultraviolet (UV) light/hydrogen peroxide system that can efficiently produce hydroxyl radicals. Fenton reaction can produce hydroxyl radical continuously assisted with UV irradiation. (Lee et al., 2003) While the ultraviolet light/hydrogen peroxide process has attracted considerable attention due to its usefulness for the purification of underground or drinking water and for the water treatment of industrial effluents (Benitez et al., 2000; Santiago et al., 2002; Zhang et al., 2003), few studies have been reported on the application of this process to the oxidation of gaseous VOCs. (Alibegic et al., 2003).

In this study, ethylene and methanethiol are used as model compounds. Ethylene was not oxidized directly under UV irradiation having a wavelength of 254 nm and it does not dissolve in a hydrogen peroxide aqueous solution. We have found that a system containing ethylene and hydrogen peroxide exhibits a characteristic phenomenon, called "light induced chemical absorption". (Sugawara, et al., 2009) UV irradiation induces the absorption of ethylene into the hydrogen peroxide aqueous solution. The oxidation behavior of methanethiol, one of the worst stench gases, was also investigated in the systems of UV/hydrogen peroxide aqueous solution and UV/hydrogen peroxide aqueous solution/wire mesh to evaluate the usefulness of UV irradiation for the oxidation of volatile organic compounds.

2. Experiment

Fig. 1 shows a schematic diagram of the rotating gas-liquid two phase photo reactor used in the present study. It comprises a pyrex glass cylinder with a volume of 3 liters (outside diameter: 130 mm, length: 250 mm) and a low-pressure mercury lamp (Nippon Photo Science, AT-1, wavelength: 254 nm, length: 360 mm, diameter: 15 mm) inserted in a fused silica tube (inside diameter: 24.8 mm). Nitrogen gas was supplied to the fused silica tube to cool the lamp. The output of the low-pressure mercury lamp was controlled by a stabilizer and an auto slidac. The irradiation length of the lamp was fixed to 125 mm in the experiment. The reactor could be rotated at a certain speed by a motor connected to a belt. The inside of the reactor wall is uniformly covered by a liquid film of the hydrogen peroxide aqueous solution due to the rotation of the reactor. After pouring the

hydrogen peroxide aqueous solution into the reactor, the gas contained within the reactor was replaced by nitrogen gas. The volume of hydrogen peroxide solution was 85 cc. A certain amount of methanethiol (Taiyo Nippon Sanso Co. 9.97% of methanethiol and N₂ balance) was supplied to the reactor. When the methanethiol concentration uniformly attained a certain value within the reactor, the rotation was started at 6 rpm and the lamp was lit. According to the preliminary experiments, the light induced chemical adsorption rate was not affected by rotation speeds more than 3 rpm. A stainless steel mesh (size: 225 mm × 334 mm, 50 mesh) was installed within the reactor shown in Fig. 1 in order to investigate the effect of Fenton reaction. The liquid and gas within the reactor were sampled after a certain time interval. The methanethiol concentration was analyzed by a gas chromatograph (Yanaco G2800) equipped with FID. The contents of carbon dioxide and total organic carbon were measured by TOC analyzer (Shimadzu TOC-5000A). The change in the hydrogen peroxide concentration was analyzed by a spectrophotometer (JASCO Model V-520). The intermediates dissolved in the hydrogen peroxide aqueous solution were analyzed by an ion chromatography (DIONEX DX120).

The pH change in the liquid phase was measured by a glass electrode pH meter (TOA-DKK HM20E). The carbon dioxide concentration in the liquid phase was determined by a method as follows: carbon dioxide was released by adding hydrochloric acid to the sample solution for lowering the pH value and bubbling with nitrogen gas, which was absorbed by barium oxide aqueous solution. The amount of carbon dioxide was calculated from the weight of precipitate of barium carbonate.

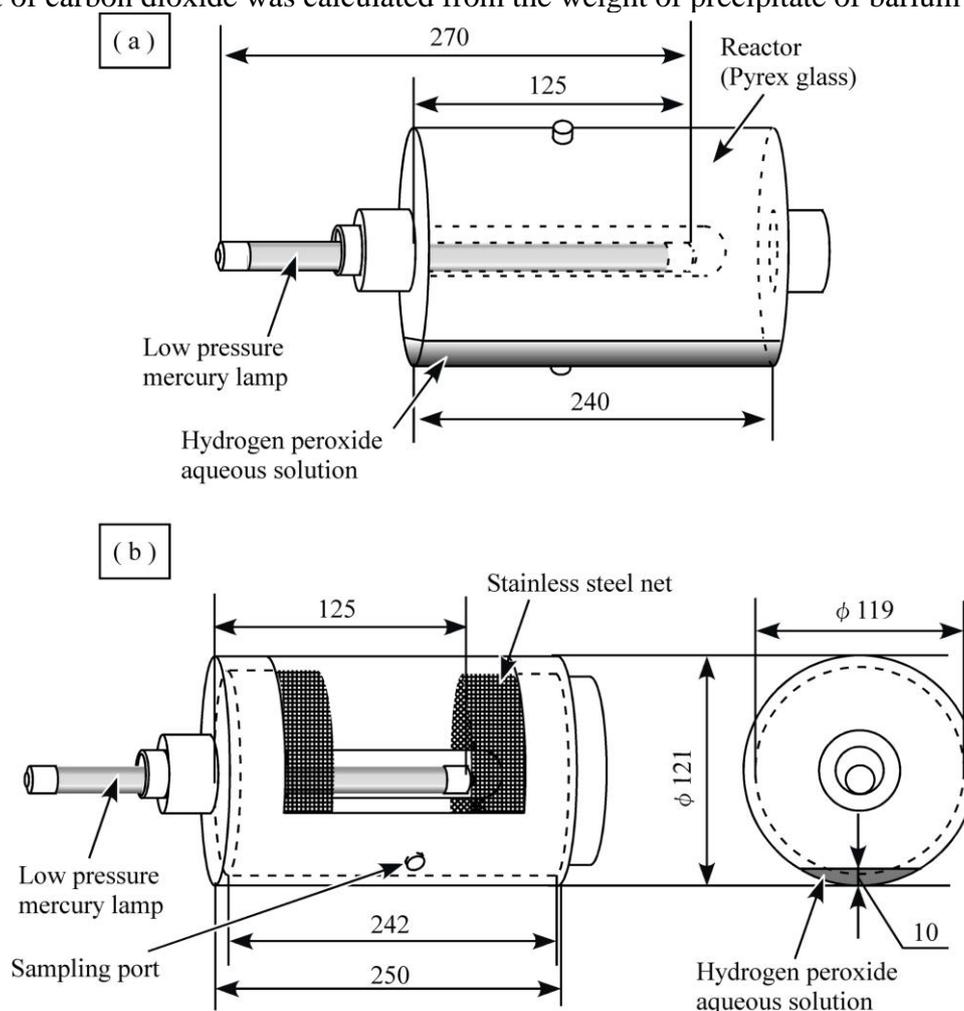


Fig.1 Schematic diagram of experimental apparatus.
 (a) UV/H₂O₂ system, (b) UV/H₂O₂/wire mesh system

3. Results and discussion

The oxidation behavior of methanethiol was investigated under the initial concentrations of methanethiol and hydrogen peroxide aqueous solution of 300 ppmV and 0.591 mol/l. Fig. 2 shows changes in methanethiol concentration, the amounts of total organic carbon and inorganic carbon expressed in the terms of carbon concentrations [mg-C/l], and hydrogen peroxide concentration under the condition with and without UV irradiation. In the period of dark condition before UV irradiation, no appreciable change was observed for methanethiol and no carbon dioxide formation was detected. The total carbon in the gas phase was consisted with the amount of methanethiol, which indicated that methanethiol existed alone before UV irradiation. It means that the direct photo-oxidation of methanethiol by hydrogen peroxide can be neglected. The methanethiol concentration began to decrease drastically with the start of UV irradiation. The total carbon content in the gas phase showed a minimum around 90 min and increased with the reaction time. The formation of carbon dioxide was not observed and the total carbon in gas phase indicated the amount of organic carbon before the disappearance of methanethiol. The total carbon in gas phase at the reaction time when methanethiol disappeared was inconsistent with the initial amount of total carbon. The concentration of the hydrogen peroxide aqueous solution did not exhibit an appreciable change; however, the pH value changed from 4.94 at the initial condition to 2.72 at the reaction time of 240 min. These results revealed that methanethiol was converted to intermediates that dissolved in the hydrogen peroxide aqueous solution.

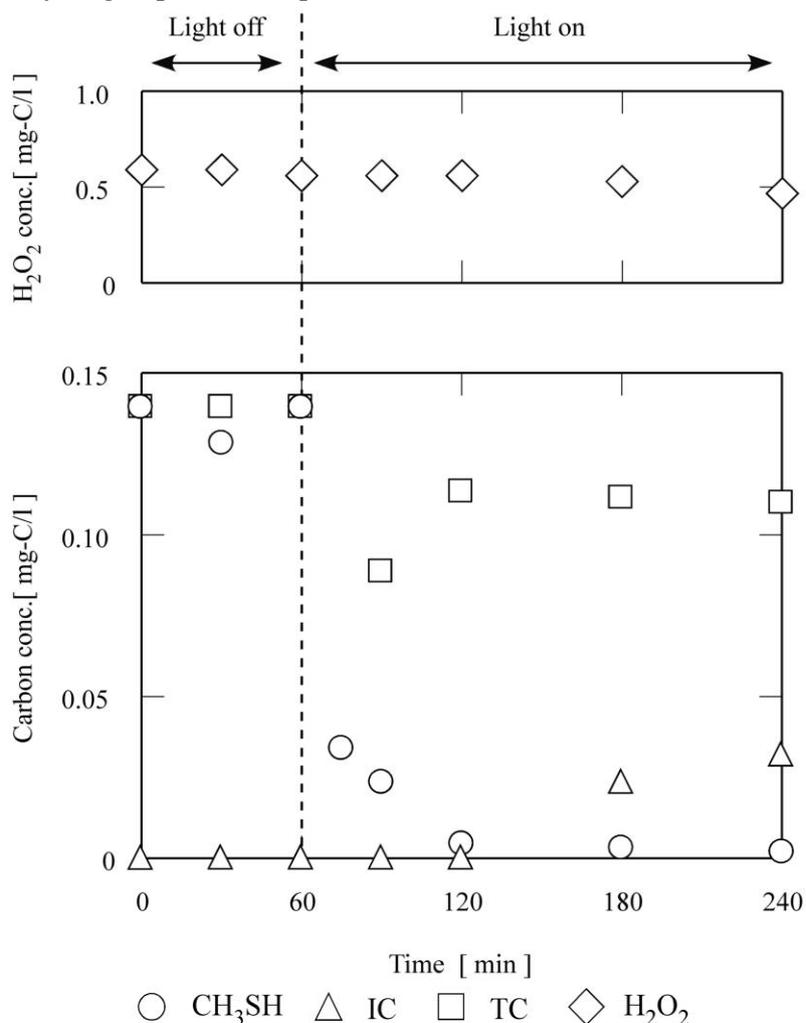


Fig.2 Sequential change in carbon component concentration in gas phase by UV/H₂O₂ oxidation process.

It was estimated that the organic carbon remained in gas phase was formed from the direct decomposition of methanethiol by UV irradiation of 254 nm (Balla and Heicken, 1985). The oxidation rate of organic compounds dissolved in the liquid phase was slow because no carbon dioxide formation was observed by 120 min. When UV irradiation was continued after methanethiol disappeared in the gas phase, carbon dioxide appeared and its amount increased with the reaction time.

4. Conclusion

The photo-oxidation behaviors of ethylene and methanethiol were investigated in ethylene gas/hydrogen peroxide aqueous solution system and methanethiol gas/hydrogen peroxide aqueous solution/wire mesh system under UV irradiation. It was found that ethylene was not oxidized by direct UV irradiation having a wavelength of 254 nm; further, it was not absorbed in a hydrogen peroxide aqueous solution under dark condition. The light induced chemical absorption of ethylene occurs when UV light irradiates the ethylene gas/hydrogen peroxide solution system. Under UV irradiation, the organic intermediates formed by the light induced chemical absorption from ethylene, were oxidized and mineralized to carbon dioxide in the hydrogen peroxide solution.

The photo-oxidation of methanethiol in the UV-H₂O₂ system indicated that the direct decomposition rate of methanethiol was larger than the oxidation rate of intermediates by hydroxyl radical in the liquid phase, showing the organic carbon remained in the gas phase. The UV/H₂O₂/Wire mesh system accelerated the oxidation of intermediates in liquid phase as well as the intermediates in the gas phase. The drastic change of methanethiol by UV irradiation was caused by multiple reactions of photo-oxidation and photo-Fenton reaction in addition to the direct photodecomposition.

5. References

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