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AB5) Method development for detecting superoxide/hydroperoxyl radical

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INTRODUCTION

HO_2 radical plays pivotal roles in the tropospheric O_3 formation chemistry. This radical oxidizes NO to NO_2 and thus HO_2 radical can lead to in-situ ozone formation. Numerous methods have been tried to measure concentrations of atmospheric HO_2 in gas phase. Detecting methods applied in the air are a chemical amplifier (Cantrell et al., 1996), FAGE (Fluorescence Assay with Gas Expansion) (Hard et al., 1984), and LIF (Laser-induced Fluorescence) (Stevens et al., 1994). These methods have been limited because of low sensitivity and interferences such as O_3, NO, and itself (Stevens et al., 1994).

In this study, the new method has been developed to determine the qualitative measurement through conversion of gaseous HO_2 radical formed in the air to liquid phase. In addition, the most important thing to measure HO_2 is time-resolved resolution because HO_2 has short life-time of minutes as an intermediate in a chemical reaction of liquid phase. Hence, HO_2 measurement should be tested using in-situ measurement.

EXPERIMENT

A schematic diagram of the newly designed apparatus is shown in Figure 1. Sample potentially containing HO_2/O_2^- is drawn into the reaction coil (PTFE, i.d., 0.8mm) from the photolysis of H_2O_2, mixed with Fe^{3+}-EDTA/BA, and then the hydroxybenzoic acid(OHBA) produced through Fenton-like reaction is measured in the fluorescence detector (Waters 474). The OHBA detection is based on the fluorescent characteristic of OHBA with a high pH (> 11), and the excitation and emission wavelengths of OHBA were set at 320nm and 400nm, respectively.

RESULTS AND DISCUSSION

The optimum conditions in this study were determined by varying effects as affected by pH, concentration of Fe^{3+}-EDTA solution, hydrogen peroxide, BA, and buffer. Solutions of Fe^{3+}-EDTA was stable to air oxidation for about 1 month under neutral pH range. Based on the observed pH and reactivity of between Fe^{3+}-EDTA and hydrogen peroxide, all subsequent experiments were performed at a [Fe^{3+}-EDTA] = 20 uM. The calibration curve for OHBA analysis was performed with 2-OHBA and 3-OHBA, based on the fluorescent characteristic of OHBA (Lee et al., 1990).

HO_2/O_2^- radicals have been produced in the UV photolysis within coil reactor of this study. Taking into consideration the recombination of radicals and Fenton-like reaction, we obtain the following reaction set, where HO_2/O_2^- used to designate whichever have reactive and depend on pK_{HO2} = 4.8:

$$H_2O_2 + hv \rightarrow 2OH \quad (1)$$
$$OH + H_2O_2 \rightarrow HO_2/O_2^- + H_2O \quad (2)$$
$$HO_2/O_2^- + HO_2/O_2^- \rightarrow H_2O_2 + O_2 \quad (3)$$
$$Fe^{3+}\text{-EDTA} + HO_2/O_2^- \rightarrow Fe^{2+}\text{-EDTA} + O_2/H_2O \quad (4)$$
$$Fe^{2+}\text{-EDTA} + H_2O_2 \rightarrow Fe^{3+}\text{-EDTA} + OH- + OH \quad (5)$$
$$OH + BA \rightarrow \text{OHBA (fluorescent products)} \quad (6)$$

Here, when realizing mechanisms as shown in reactions 1 - 6, Fe^{3+}-EDTA is added in sufficient quantity to convert the HO_2/O_2^- to OH before the chain reactions of reactive radicals. Reaction (4) with $k_4 = 2 \times 10^6\ M^{-1}\ s^{-1}$ is a effectiveness of dismutation at concentration of $O_2 < 10^{-6}$ M (Bull et al., 1983). From the consequent reaction, the formed Fe^{2+}-EDTA reacts with hydrogen peroxide producing OH radical. Then the OH radical produces OHBA by means of reactions.

We have developed the usage of the Fenton-like reaction as an analytical tool for the measurement of HO_2/O_2^-. Final results including experimental results and discussions will be presented during the presentation.

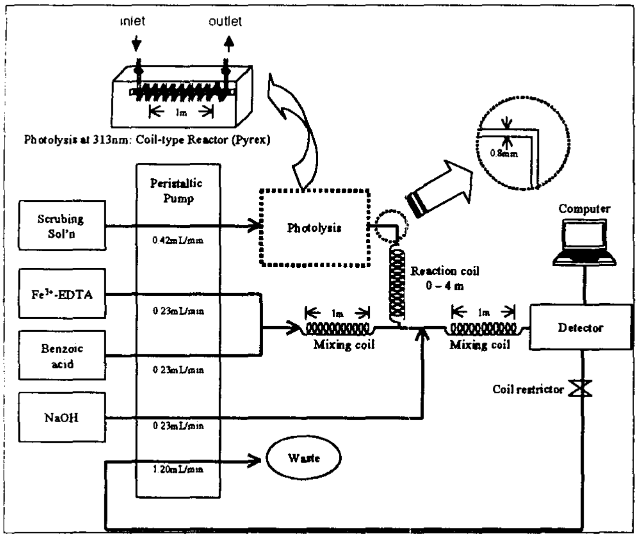

Figure. 148. The schematic diagram.

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