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2B4) Effect of Initial Concentration Ratio of Toluene/NO_x on the Photochemical Reaction in Twin Smog Chambers Filled with the Ambient Air

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1. Introduction

During the summer afternoons, the fine particles formed by photochemical reactions could contribute visibility reduction. The formation and growth of secondary ambient aerosols might be affected by primary air pollutants and by meteorological factors. In this work, the photochemical reaction of Seoul ambient air was investigated in indoor smog chambers. Since the quality of ambient air changed with time, the twin chambers were utilized to differentiate the effect of initial concentration ratio of toluene/NO_x on the formation of ozone and aerosols during the photochemical reaction (Kim et al., 2004; Bae et al., 2003).

2. Experimental

The experiments of photochemical reaction of ambient air were conducted in two identical smog chambers. Each chamber consisted of a housing, a Teflon film bag, 64 blacklights, and injection and sampling ports. The bag, made of 2-mil thick FEP Teflon film, was installed in a temperature-controlled, particle-free cleanroom facility. The volume of the cubic bag was about 5.8 m^3 (1.8x1.8x1.8 m), and the surface-to-volume ratio was 3.3 m^{-1}. During the experiment, O_3, NO-NO_2-NO_x, SO_2, and CO concentrations were measured every minute with continuous analyzers. Toluene concentration was also measured every 25 minutes by gas chromatography and an FID detection (GC/FID, Agilent Technologies model 6890N), using a 0.32 mm x 30 m x 0.25 μm HP-5 column (Agilent). The sample was concentrated with a preconcentrator (Entech model 7100) to detect toluene concnetrations of less than 1 ppm. The particle size distribution was measured every 5 minutes using a scanning mobility particle sizer (SMPS, TSI model 3934U).

Prior to each experiment, the Teflon bags were flushed with purified air to minimize the effect of bag contamination, and then background reactivity of the bags was confirmed to be low through the photochemical reactions of purified air for several hours. For main experiments, the air in each bag was exchanged with ambient air three times to initialize the bags. Thereafter, the bags were filled with ambient air for about 12~30 minutes. The left chamber was filled with the unfiltered ambient air, on the other hands, the right chamber was filled with the controlled ambient air. The toluene concentration was reduced using a charcoal filter (Osaka gas FN-100PS-10), or increased by injection of a pure liquid toluene with a micro syringe.

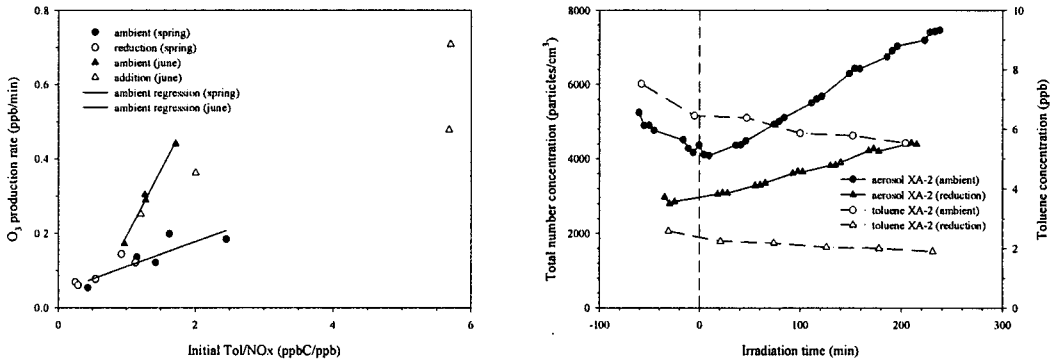
3. Results and Discussion

The experiments were done from March to June 2004, so we divided experiments into spring and summer groups. The ambient ozone production rates were proportional to the initial concentration ratio of toluene/NO_x in both of spring and June as shown in Fig. 1(a).

The increment of ozone production rates according to the ratio of toluene/NO_x in June was greater than that in March. It seems to be the seasonal difference in gaseous pollutants emission and the sunshine duration. We divided all experimental results into X (spring) and Y (summer) groups by experimental dates and again into A and B groups by the change in

tendency of aerosol concentration between twin chambers. When the effect of toluene reduction or toluene addition was clearly observed, the experiments were classified as group A, otherwise, as group B.

As an example of XA group, the irradiation time-series data of toluene and aerosol number concentrations for the XA-2 was plotted in Fig. 1(b). The initial toluene concentration at a right chamber (reduction chamber) was about 60% of that at a left chamber (ambient chamber) for XA-2, so that the ratio of toluene/NO_x decreased from 2.5 at a ambient chamber to 1.1 ppbC/ppb at a reduction chamber.



(a) Ozone (b) Particle

Fig. 1. Effect of initial concentration ratio of toluene/NO_x (ppbC/ppb).

In the case of XA-2 the toluene reduction made the relatively less ozone production rate as about 33% of that at ambient chamber, the relatively less formation of aerosol as about 39% in number concentrations and the relatively less growth of aerosol.

The initial toluene concentration at a right chamber (addition chamber) in the group of YA (addition) became higher as much as 3~32 ppb than those at a left chamber by addition of toluene during the introduction of ambient air. So the initial concentration ratio of toluene/NO_x at an addition chamber became higher than that at an ambient chamber. The toluene addition made the relatively more ozone production rate, and the relatively more formation and growth of aerosol, which is consistent with the tendency of experiments on toluene reduction. However, the effect of initial toluene concentration on the particle formation was not clearly observed when initial NO_x concentration was relatively high.

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