

## Diurnal variations in aromatic hydrocarbons in urban air of Nagoya

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The sources of aromatic hydrocarbons (AHCs) are automobile exhaust and solvent use, and urban area is thought to be the major source area. AHCs are generally reactive with OH radicals as compared to other NMHC species with OH. Hence AHCs are thought to be one of major precursors of ozone and secondary organic aerosols in and around urban area, and many experiments of AHCs as well as other non methane hydrocarbons (NMHCs) have been carried out. However these experiments covered only limited periods, and no information particularly regarding the seasonal variations in the oxidation of AHCs. Continuous measurements of NMHCs at every 3 hours were carried out in urban air of Nagoya from December 2003 to November 2004 and we attempted to obtain the information of AHCs oxidation by analyzing the diurnal variations in the molar ratios of selected AHCs for one year.

Detail documents of our measurements are described elsewhere such as our submitted paper (Saito et al., submitted to Atmospheric Environment). AHCs analyzed in this study are *m,p*-xylene, ethylbenzene, *o*-xylene, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene. High concentrations were observed during the nighttime and early morning and then decreased to minimum values at 15:00LT in their diurnal variations.

Then following five sets of pairs were made, that is, *m,p*-xylene/ethylbenzene, *o*-xylene/ethylbenzene, *m,p*-xylene/*o*-xylene, *m,p*-xylene/3-ethyltoluene, 2-ethyltoluene/4-ethyltoluene. The differences of the reaction rate constant of AHC with OH ( $k_{OH}$  (298K)) within these pairs ranged from  $0.1 \times 10^{-12} \text{cm}^3 \text{molec}^{-1} \text{sec}^{-1}$  to  $12 \times 10^{-12} \text{cm}^3 \text{molec}^{-1} \text{sec}^{-1}$ . These molar ratios were high during the nighttime and early morning and minimum at around 12:00LT not at 15:00LT.

To quantitatively estimate the daytime decreases in the molar ratios, the ratio of the molar ratio at 12:00 to those at 06:00LT were calculated (hereafter R12/R06). As the difference of  $k_{OH}$  become larger, R12/R06 become smaller, that is, the daytime decrease in the molar ratio become larger.

Moreover R12/R06 of each pair was low in summer and high (around 1.0) in winter, showing that daytime decreases of these ratios were larger in summer and smaller in winter.

To minimize the other effect than oxidation, two sets of pairs such as 2-ethyltoluene/*m,p*-xylene and 4-ethyltoluene/*m,p*-xylene were selected because the  $k_{OH}$  of 2-ethyltoluene is close to that of 4-ethyltoluene. Analyzing the correlation plot of  $\ln(2\text{-ethyltoluene}/m,p\text{-xylene})$  vs  $\ln(4\text{-ethyltoluene}/m,p\text{-xylene})$  gives us some useful information for estimating oxidation conditions of the AHCs in urban air.