## The Kinetics of Gas-phase Reactions of Selected Monoterpenes and Cycloalkenes with Ozone and Nitrate Radicals Studied by Headspace Solid-Phase Microextraction (HS-SPME)

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Oxidation of volatile organic compounds in the troposphere is primarily initialised by hydroxyl radicals, ozone, and nitrate radicals, NO<sub>3</sub>, with the dominant degradation route being determined by the relative concentrations of the oxidants as well as the rate coefficients for the reactions of the oxidised compounds with these species<sup>(1)</sup>. In this study, a novel variant of the relative rate method has been employed to measure the room-temperature rate coefficients for the gas-phase reactions of ozone and NO<sub>3</sub> with selected monoterpenes and cycle-alkenes with structural similarities to monoterpenes. Measurements were carried out at  $298 \pm 2$  K and  $760 \pm 10$  Torr. The experimental results were obtained by combining headspace solid-phase microextraction (HS-SPME) sampling with gas chromatography-mass spectrometry (GC-MS) detection. The experimental set-up is depicted in Fig.1. Fig. 2 (a) illustrates the HS-SPME calibration for  $\alpha$ -pinene while Fig.2 (b) gives an example of a kinetic plot used for derivation of the rate coefficients.



Figure.1: Experimental set up for combining HS-SPME with GC-MS analysis.

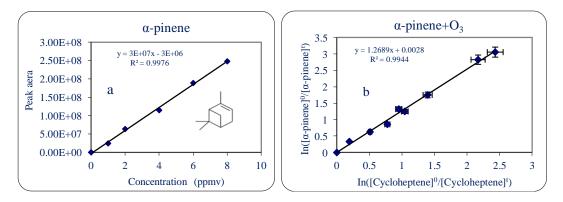


Figure 2 (a & b): (a): Calibration of  $\alpha$ -pinene using HS-SPME and (b) Relative rate plot reacting  $O_3$  with  $\alpha$ -pinene vs. cyclohepten ( Reference compound ).

## **References.**

1- B.J. Finlayson-Pitts and J.N. Pitts Jr., *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego, 2000.