Pressure Dependent HO_2 Calibration of the Fluorescence Assay by Gas Expansion (FAGE) Instrument Using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)

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The hydroxyl (OH) and hydroperoxy (HO_2) radical are very important tropospheric radical species. The balance between OH and HO_2 (the HO_x cycle) can give understanding of localised atmospheric composition. OH and HO_2 is measured in both ground and aircraft based campaigns using FAGE. Calibration of this non-absolute fluorescence technique is traditionally achieved by H_2O photolysis.[1] Operation of FAGE at varying pressure can affect the instrument sensitivity to HO_x due to internal fluorescence cell pressure changes. These are traditionally accounted by varying the inlet pinhole size of the instrument, however this may alter the gas expansion and hence the instrument sensitivity to OH and HO_2.

Presented here are the initial results from an independent HO_2 pressure dependent calibration method using the stainless steel HIRAC chamber, which can operate at various pressures (0.1 – 1 bar). Formaldehyde, HCHO, is photolysed ($\lambda < 245$ nm) in the presence of O_2 to form $2HO_2$ to steady state, and the post-photolysis HO_2 decay is monitored using FAGE.

The decay is a function of the second order HO_2 self reaction, for which the rate is well known. As $[HO_2] = S_{HO2} \times C_{HO2}$ (FAGE HO_2 signal and instrument sensitivity, respectively), the second order rate equation can be rearranged to give (1) and a plot of $1/S_{HO2}$ vs. time yields C_{HO2} (Fig. 1).

$$\frac{1}{(S_{HO_2})_t} = \frac{1}{(S_{HO_2})_0} + \frac{2k_{HO_2+HO_2}\, t}{C_{HO_2}} \qquad \textbf{(1)}$$

Initial results from both pressure dependent calibrations were good agreement (Fig. 2), validating the widely used traditional "wand" calibration method, supporting field-work and chamber based HO_2 measurements.

THURSDAY

References

(1) Faloona *et al.*, *J. Atmos. Chem.*, **2004**, 47, 139-167
(2) R. Atkinson, Atmos. Chem. Phys, **2004**, 4, 1461-1738

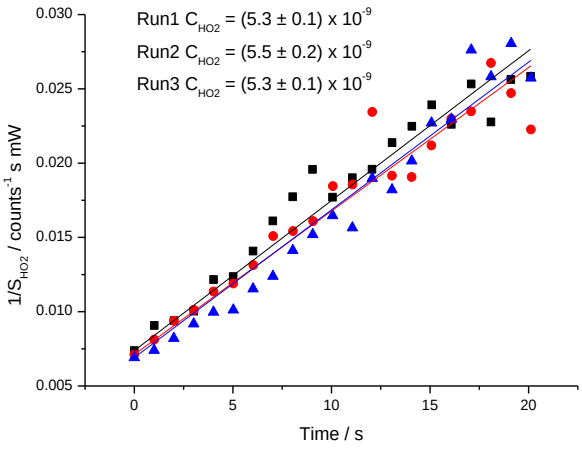

Fig. 1: Second order plot of $1/S_{HO2}$ vs. Time used to determine C_{HO2} ($P_{internal}$ = 1.6 Torr).

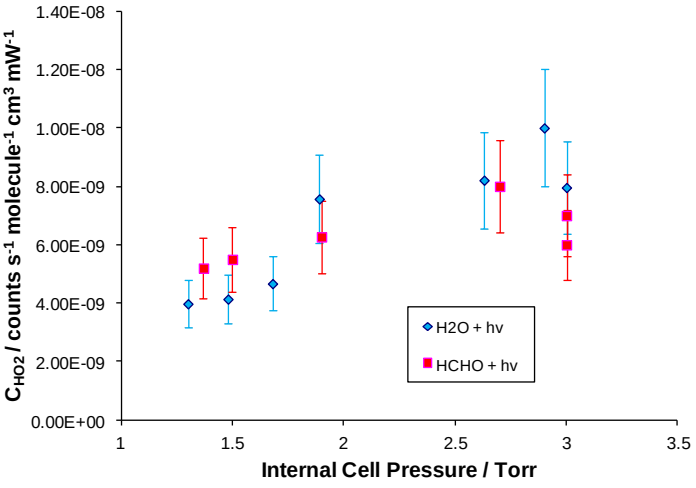

Fig. 2: Comparison of the pressure dependent H_2O photolysis and HCHO photolysis calibration techniques.