Henry's law coefficients and hydrolysis rate coefficients of

atmospheric trace gases <u>Ranajit K. Talukdar</u>,^{1,2,*} Bartlomiej Witkowski, ^{1,2,3} A. R. Ravishankara², and James B. Burkholder

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Solubility coefficients of gases in liquids (Henry's law constant, H) and rate coefficients for the hydrolysis of molecules in the liquid phase (k) of atmospheric trace gases are needed to model and quantify their aqueous-phase processing. We built an experimental apparatus to measure Henry's law solubility coefficients of weakly soluble atmospherically relevant compounds and, in applicable cases, their hydrolysis rate coefficients. The apparatus, shown schematically in Fig 1, consists of a closed-cycle bubble reactor combined with a Fourier transform infrared (FTIR) spectrometer that was used to measure the gas phase concentration of the dissolving gas and products of hydrolysis reaction. Results from experiments with perfluoro-2-methyl-3-pentanone (C₂F₅C(O)F(CF₃)₂, PFMP) and perfluoro-2-methyl-3-butanone (CF₃C(O)CF(CF₃)₂, PFMB) will be presented. PFMP is currently being used as a fire suppressant in place of Halons, which have high ozone depletion potentials (ODP); PFMP and PFMB have essentially zero ODPs. The tropospheric photolysis lifetime of PFMP is relatively short, on the order of several weeks; thus, this molecule has a small Global Warming Potential (GWP). However, the hydrolysis of PFMP is known to produce HFC-227ea (CF₃CHFCF₃), a molecule that has low solubility, an atmospheric lifetime of 38.9 years, and a GWP of 3580 (100 year time horizon). Therefore, the atmospheric aqueous-phase processing of PFMP to produce HFC-227ea, even if only a minor loss pathway, can lead to a very large GWP attributable to its emission. To validate our methodology, the Henry's law solubility constants for SF₆, CF₃CHF₂ (HFC 134a), and $C_2F_5CF(CF_3)_2$ (HFC 227ea), molecules that have well established H values and extremely low hydrolysis rate coefficients, were also measured. The results of these measurements will be presented and atmospheric implications of these findings discussed.



Fig. 1 Experimental setup