

Nonmethane Hydrocarbon Measurements at Barrow and Samoa

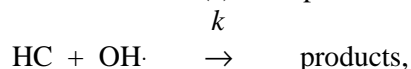
D. R. Blake and F. Sherwood Rowland

Department of Chemistry, 516 Rowland Hall, University of California, Irvine 92697 2025; 949-824-4195; Fax 949-824-2905; E-mail: dblake@orion.oac.uci.edu

For our latitudinal trace gas survey, the sampling strategy is to collect approximately 60-80 whole air samples during a 3-week period in 40-45 locations four times a year (usually March, June, September, and December). Of these, four are collected in Barrow (usually over a 2-3 day period by our research group members) and three samples are collected in Samoa during a 2-3 week period, by station personnel. The air samples are collected in conditioned, evacuated 2-L stainless steel canisters equipped with a single stainless steel bellows valve. During sampling, the canister is filled to ambient pressure over a period of about 1 minute. At the end of the collection period, the sampling canisters are returned to the UCI laboratory for analysis.

Our current trace gas analytical configuration is a three-gas chromatograph (Hewlett-Packard 6890), five-column (DB-1, DB-5, DB-5, PLOT, and Rtx-1701), five-detector (2 FIDs, 2 ECDs, 1 MSD) analytical system that is calibrated to quantify over 200 halocarbons, NMHCs, and alkyl nitrates. However, only a fraction of these trace gases (about 40) are routinely present at the remote collection sites of the latitudinal survey.

The main sink of nonmethane hydrocarbons (NMHCs) is through photooxidation, initiated by reaction with OH· radicals. The lifetime (τ) of a species HC, as a result of reaction with the hydroxyl radical,



is

$$\tau_{\text{HC}_{\text{OH}}} = \frac{1}{k[\text{OH}\cdot]}$$

where k is the laboratory determined reaction rate constant. Unsaturated hydrocarbons, such as the alkenes, also undergo addition reactions with ozone.

Individual ethane mixing ratios for the Barrow and Samoa stations collected between March 1996-June 2000 are shown in the figure plotted versus day of year. The average lifetime of ethane is 2-3 months and most of the ethane emissions are in the NH. This leads to a substantial N/S gradient in concentration and to lower mixing ratios during each hemisphere's summertime, when photochemistry is most active. Unlike the other sites in the UCI monitoring network, the Barrow and Samoa sampling locations are fixed at the CMDL stations. As a result, the mixing ratios measured at these sites are sometimes elevated as a result of local contamination. At Barrow, local contamination can occur when the prevailing wind is from the direction of town rather than from the ocean or tundra. This local effect is evidenced by the greater year-to-year variability in the Barrow ethane concentrations. Our near term plan is to increase the Barrow and Samoa sampling frequency to once/week. This higher frequency data combined with the even higher frequency data of CMDL will be used to determine if atomic chlorine concentrations are great enough to affect regional oxidation of specific trace gases.

