1. MEASUREMENTS

The hydroxyl and hydroperoxy radicals (OH and HO\textsubscript{2}, collectively referred to as HO\textsubscript{3}) are extremely reactive species, causing most of the photochemical processing of trace gases in the atmosphere and influencing both ozone production and aerosol formation.

OH and HO\textsubscript{2} were observed during the TexAQS campaign in Houston in August/September 2000 with the Penn State GTHOS instrument (Ground-based Tropospheric Hydrogen Oxides Sensor) by laser induced fluorescence of OH. A detailed description of the technique is given in Stevens (1994). HO\textsubscript{2} was quantitatively converted to OH by titration with NO. The 1σ precision for OH was about 2.5×10\textsuperscript{-5} molec/cm\textsuperscript{3} for 10-min averages or approximately 0.01 ppt. For HO\textsubscript{2}, the 1σ precision was approximately 0.1 ppt for 1-min averages. The 2-sigma-accuracy was ±40%, due to uncertainties of the absolute calibration.

In addition total OH loss rates in ambient air were measured using the TOHLM experiment (Total OH Loss rate Measurement). OH produced by photolysis of water vapour is injected at different positions into ambient air pumped through a flow tube. The remaining OH at the end of the flow tube is measured by LIF. The slope of the OH signals plotted versus reaction time then gives the reaction rate of OH. A detailed description of the instrument can be found in Kovacs (2001). The total uncertainty for the measurements is estimated to ±25%.

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2. RESULTS

Mean midday values for OH were about 7×10\textsuperscript{6} molecules/cm\textsuperscript{3} and 10 ppt for HO\textsubscript{2}. The diurnal development of HO\textsubscript{x} shows strong dependencies on NO\textsubscript{3} and other trace gases. NO\textsubscript{3} mixing ratios were typically higher in the morning, leading to lower HO\textsubscript{2} mixing ratios in the first half of the day.

Comparison with results from the Southern Oxidants Study, which took place in Nashville the summer before, show that, even though the OH concentrations were similar at both urban sites during daytime and the HO\textsubscript{x} production rate from ozone photolysis was about 1.5 times higher in Houston, HO\textsubscript{2} mixing ratios were much lower in Houston than in Nashville (Fig. 1).

The OH loss rate through reaction with NO\textsubscript{2} was usually several times smaller than the measured total reaction rate of OH. Thus each OH radical reacted several times with hydrocarbons forming HO\textsubscript{2}, which was then reconverted to OH by reaction with NO\textsubscript{3} before reacting with NO\textsubscript{2} to form nitric acid. This chain length was about 30% lower in Houston during daytime than in Nashville, indicating different composition of hydrocarbons at the two sites and a relatively more important HO\textsubscript{x} sink by reaction of OH with NO\textsubscript{2} in Houston. Additionally, reaction of OH with hydrocarbons frequently leads to formation of formaldehyde, which photolyzes to produce HO\textsubscript{2}. Therefore the difference in chain length possibly explains the different HO\textsubscript{x} mixing ratios at the two sites.

Reaction of HO\textsubscript{2} with NO produces NO\textsubscript{2}, which is photolysed during daytime leading to ozone production. According to the lower HO\textsubscript{2} mixing ratios in Houston, ozone production from this mechanism was about half in Houston than in Nashville. However the total ozone production rates cannot be calculated due to the lack of RO\textsubscript{2} measurements at both sites. As would be
expected, the ozone production rate from HO\textsubscript{2} and NO reaction for any given NO mixing ratio was highest for highest HO\textsubscript{2} production rates. However, for constant P(HO\textsubscript{x}) no decrease of the ozone production rate was observed at high NO\textsubscript{x}, when P(O\textsubscript{3}) should be NO\textsubscript{x} saturated. This could be due to HO\textsubscript{2} sources emitted along with NO, so that the increased HO\textsubscript{2} sources compensate for the increased NO\textsubscript{x}-induced losses. If this is not the case, more O\textsubscript{3} may be produced in high NO\textsubscript{x} plumes than is currently being calculated by atmospheric models.

The measurements indicate that both species were also sometimes present at night. HO\textsubscript{2} occasionally reached more than 10 ppt in air with high alkene and ozone concentrations, indicating nighttime production of HO\textsubscript{2} through ozonolysis of alkenes.

Further testing of our understanding of the sources and sinks of HO\textsubscript{2} can be accomplished by comparison of the measured loss rates with the expected production rates. The measured loss rates are usually significantly higher than OH production rates calculated from photolysis of O\textsubscript{3} and conversion of HO\textsubscript{2} by reaction with NO, indicating the existence of additional production or conversion mechanisms contributing several 10\textsuperscript{7} OH radicals per second.

Figure 1. Mean diurnal variations for OH, HO\textsubscript{2}, P(HO\textsubscript{x}) due to O\textsubscript{3} photolysis and P(O\textsubscript{3}) due to reaction of HO\textsubscript{2} and NO for SOS 99 and TEXAQS. The error bars show the standard variation of the hourly means.

REFERENCES
