9.7   OH AND HO_2 CONCENTRATIONS, PRODUCTION AND LOSS RATES
AT THE LA PORTE SITE DURING TEXAQS 2000

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1. MEASUREMENTS

The hydroxyl and hydroperoxy radicals (OH and HO_2, collectively referred to as HO_x) 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_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_2 was quantitatively converted to OH by titration with NO. The 1σ precision for OH was about 2.5×10^5 molec/cm^3 for 10-min averages or approximately 0.01 ppt. For HO_2 the 1σ precision was approximately 0.1 ppt for 1-min averages. The 2-sigma-accuracy was $\pm40\%$, due to uncertainties of the absolute calibration.

In addition total OH loss rates in ambient air were measured using the TOHLM expe-riment (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 $\pm25\%$.

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2. RESULTS

Mean midday values for OH were about 7×10^6 molecules/cm^3 and 10 ppt for HO_2. The diurnal development of HO_x shows strong dependencies on NO_x and other trace gases. NO_x mixing ratios were typically higher in the morning, leading to lower HO_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_x production rate from ozone photolysis was about 1.5 times higher in Houston, HO_2 mixing ratios were much lower in Houston than in Nashville (Fig. 1).

The OH loss rate through reaction with NO_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_2, which was then reconverted to OH by reaction with NO, before reacting with NO_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_x sink by reaction of OH with NO_2 in Houston. Additionally, reaction of OH with hydrocarbons frequently leads to formation of formaldehyde, which photolyses to produce HO_2. Therefore the difference in chain length possibly explains the different HO_x mixing ratios at the two sites.

Reaction of HO_2 with NO produces NO_2, which is photolysed during daytime leading to ozone production. According to the lower HO_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_2 measurements at both sites. As would be

expected, the ozone production rate from HO_2 and NO reaction for any given NO mixing ratio was highest for highest HO_x production rates. However, for constant $P(HO_x)$ no decrease of the ozone production rate was observed at high NO_x, when $P(O_3)$ should be NO_x saturated. This could be due to HO_x sources emitted along with NO, so that the increased HO_x sources compensate for the increased NO_x-induced losses. If this is not the case, more O_3 may be produced in high NO_x plumes than is currently being calculated by atmospheric models.

The measurements indicate that both species were also sometimes present at night. HO_2 occasionally reached more than 10 ppt in air with high alkene and ozone concentrations, indicating nighttime production of HO_x through ozonolysis of alkenes.

Further testing of our understanding of the sources and sinks of HO_x 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_3 and conversion of HO_2 by reaction with NO, indicating the existence of additional production or conversion mechanisms contributing several 10^7 OH radicals per second.
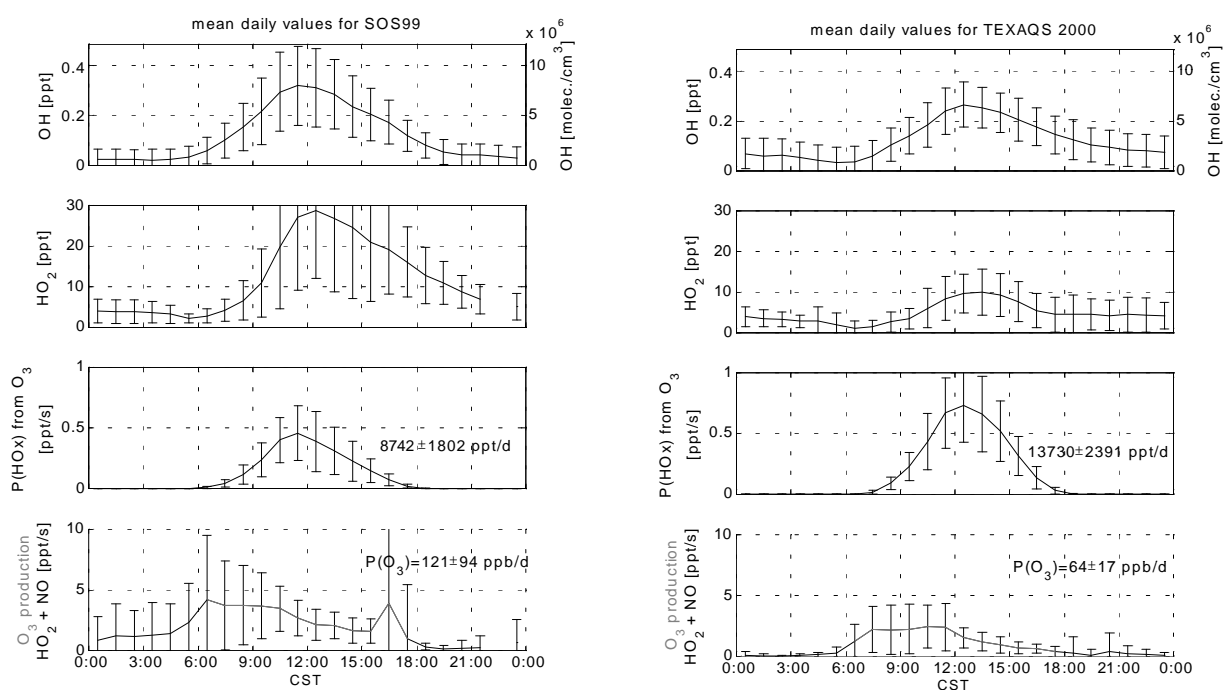

Figure 1. Mean diurnal variations for OH, HO_2, $P(HOx)$ due to O_3 photolysis and $P(O_3)$ due to reaction of HO_2 and NO for SOS 99 and TEXAQS. The error bars show the standard variation of the hourly means.

REFERENCES

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