DIURNAL VARIATION OF THE CONCENTRATION OF OH DURING THE 27TH NOVEMBER 1999 AT THE SONNBLICK OBSERVATORY (3106 M A.S.L.)

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PTR-MS APPLICATION - TROPOSPHERIC OH

ABSTRACT

Using PTR-MS (LINDINGER et al) we measured the densities of several VOCs at the Sonnblick Observatory from November 27th to December 1st, 1999. On November 27th during daytime the concentrations showed a substantial decline, of about 50% in the case of pentenol, one of the most prominent VOCs present. The meteorological situation was characterized by strong inversion and very little wind activity. Thus any changes in VOC concentrations observed were solely due to reaction kinetics without significant influence of transport phenomena.

Assuming that reaction with OH radicals is the main loss process for pentenol (k=6x10-11cm3/s) we calculated the OH radical density as dependent on time. The concentration increased from zero at 8:00 local time to a maximum density of 1.6E6 cm3 at 11:00 and declined thereafter reaching zero level at 15:00. This variation coincided well with the time dependence of solar radiation.

RESULTS

Densities of volatile organic compounds measured at the Sonnblick Observatory using PTR-MS.

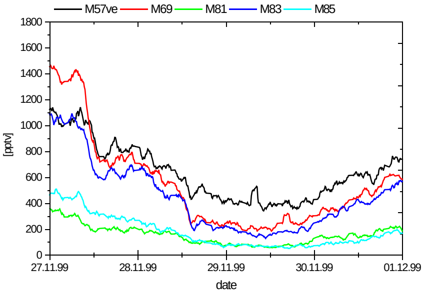


Fig.1: Concentrations measured by means of GC-PTR-MS. The compounds were identified as follows: 2(E)-hexenal (M57 plus fraction of M99), pentenol (M69), 3(Z)-hexenal (M81 plus fraction of M99), hexenol plus hexanal (M83) and ethylvinylketone

Meterological data (see e.g. Fig.2 and 3) show that during 27th of November there was very little movement of the air, strong inversion, and thus no exchange of VOCs in the vicinity of the top of the Sonnblick. Therefore the decline of the observed VOC densities during daytime is mainly due to reactions of these VOCs with OH-radicals.

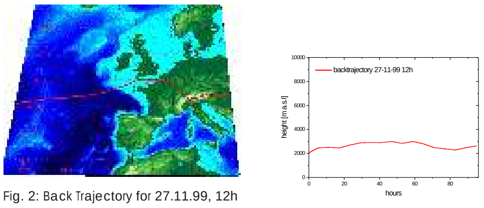


Fig. 2: Back Trajectory for 27.11.99, 12h

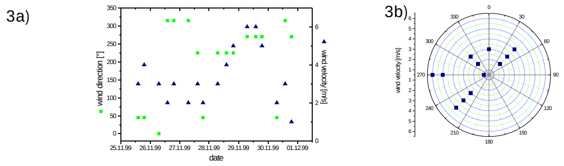


Fig 3a,b: Average wind velocity and wind direction

$$CCCCCC(O)H + OH \longrightarrow products$$

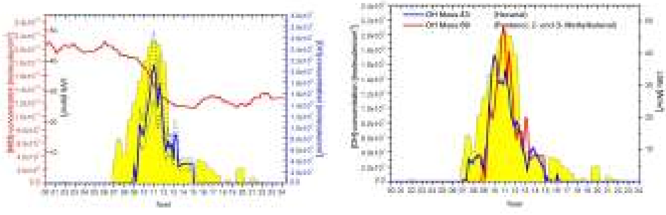
$$k_{hexanal}(-3°C) = (3.0 \pm 0.6)\ 10^{-11}\ cm^3/s$$

$$CCC(OH)C = C + OH \longrightarrow products$$

$$k_{mass69}(-3°C) = (3.5 \pm 0.6)\ 10^{-11}\ cm^3/s$$

$$[OH] = \frac{1}{k_{VOC}\ [VOC]_t}\ \frac{d[VOC]}{dt}$$

Using these reactions we calculated the OH densities from the density variation of two VOCs (taken from Fig 1) as shown in Fig 2a, b.



OH radicals on the 27-11-99

Diurnal concentrations of OH radicals

Fig.2a,b: Calculated OH-densities together with measured intensity of UV-radiation during Nov 27th,1999

Mixing ratios for Aldehydes on the 27-11-99

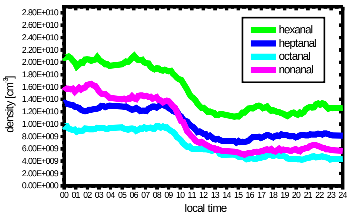


Fig. 3: Densities of various aldehydes

Using OH-concentrations as shown in Fig 2a,b and density variations of the aldehydes heptanal, octanal and nonanal respectively we calculated reaction rate constants for the reactions of OH with these aldehydes,
k~3.3E-11 cm3sec-1 (heptanal),
k~3.8E-11 cm3sec-1 (octanal) and
k~4.5E-11 cm3sec-1 (nonanal).
These values follow quite well a progression of known rate constants for lower aldehydes (see fig. 4).

Rate constants with OH for Aldehydes at -3°C

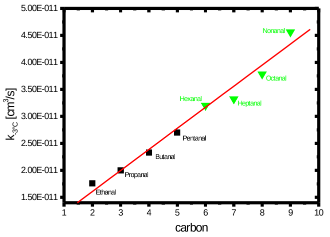


Fig 4: Progression of rate constants taken from the literature (butanal to hexanal) and presently obtained rate constants (heptanal to nonanal)

REFERENCES

Fall R., T. Karl, A. Hansel, A. Jordan, W. Lindinger; Volatile organic compounds emitted after leaf wounding: On-line analysis by proton-transfer-reaction mass spectrometry; JGR, Vol 104, 15963-15974, 1999

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CONCLUSION

- OH density on the 27-11-99:
  1.6 to 2 x 10^6 cm^{-3}
- Rate constants of OH for reactions with higher aldehydes were obtained

ACKNOWLEDGMENTS

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