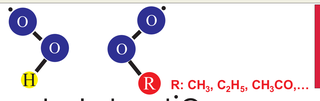
Xy151

EGU-2011 Vienna

A modified PeRCA instrument for the selective determination of atmospheric concentrations of HO_2 and RO_2 radicals

Anna Chrobry, M.D. Andrés Hernández, Deniz Kartal, and John P. Burrows
University of Bremen, Institute of Environmental Physics, Postbox 330440, D-28334 Bremen
e-mail: achrobry@iup.physik.uni-bremen.de

Peroxy radicals



Peroxy radicals are radicals characterized by a oxygen-oxygen single bond $^{\cdot}O_2$ group. Hydroxyl- and organylperoxyl- radicals, HO_2 and RO_2 respectively, where R refers to an organic chain, play a crucial role in the photo-oxidation processes in the troposphere, in particular in the formation and depletion of tropospheric ozone.
They are produced mainly via the oxidation of hydrocarbons and CO by OH radicals.
For this research peroxy radical chemical amplification (PERCA) technique is used to measure peroxy radicals.

Measurement technique

PERCA measures the total sum of HO_2 and RO_2 radicals, $RO_2^{*}=HO_2+\Sigma RO_2$ through conversion and amplificattion into NO_2 by adding NO and CO to the sampled air at the entrance of the reactor.
The amplification factor is called Chain Length (CL) and results from the competition between amplification, chemical loss reactions and wall losses (see Fig.1). CL and depends on:

a) concentration of the reactants CO and NO;
b) reactor volume, i.e., sample residence time
c) reactor material and shape, i.e., heterogenous losses
d) relative humidity

$$CL = \frac{[\Delta NO_2]}{[RO_2^{*}]}$$

$$RO_2^{*} = HO_2 + \Sigma RO_2$$

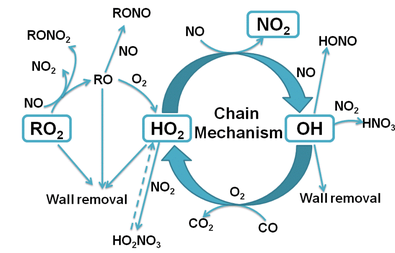


Figure 1 : Amplification cycle and main loss reactions of the chemical amplification method

Radical speciation

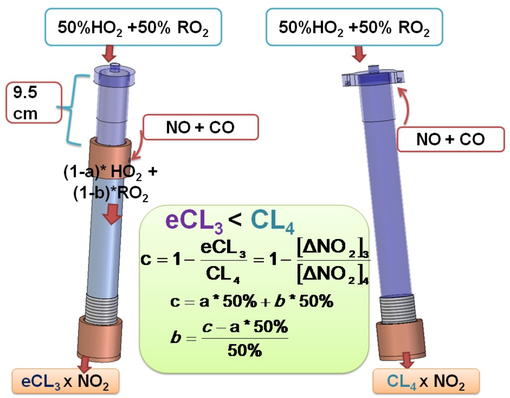


*Figure 3: Determination of RO_2 radical removal coefficient **b***

In this research selective measurement of radicals is proposed based on the HO_2 greater wall loss rate comparing to RO_2 [1,2,3]. A novel reactor to measure solely RO_2 was constructed varying the position of the addition point of NO and CO (Fig. 2 and 3). Within the 9.5 cm of the new reactor up to 99% of HO_2 is expected to be removed prior to reaching the addition points of CO and NO (see Fig. 4). Removal efficiency of HO_2 and RO_2 radicals in a novel reactor can be quantified if the coefficients **a** and **b** are calculated (Fig. 2-3).

In each reactor radicals are partly lost due to the wall losses and radical radical reactions before they reach the amplification and conversion zone. Thus, the produced NO_2 corresponds to a lower mixing ratio of radicals participating in the amplification than that produced at the source (i.e., (1-a)*HO_2+ (1-b)*RO_2; where ***a*** and ***b*** are the removal coefficients for HO_2 and RO_2 respectively).

As CL is calculated according to the calculated amount mixing ratio of radicals produced at the source, the obtained CL is an effective chain length (eCL), which is lower than the actual CL. In case of the non modified reactor the potential losses of radicals before reaching the addition point are considered to be negligible. Therefore CL_2 and CL_4 can be assumed to be close to the actual chain length.

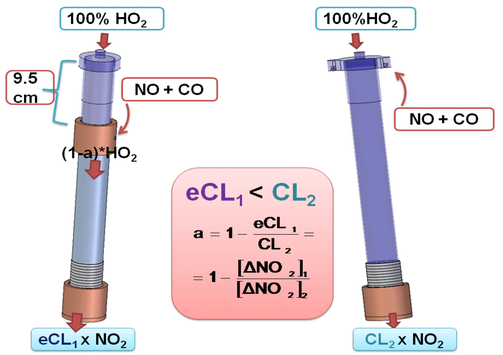


*Figure 2: Determination of HO_2 radical removal coefficient **a***

Radical losses

Radical wall losses depend on surface material properties. It has been shown that coating the reactor surfaces with Teflon reduces radical wall losses and increases the sensitivity of the PERCA technique [3]. Therefore in laboratory two identical reactors made of stainless steel covered by different inert materials (Fig. 4), i.e., amorphous silicon (A,B) and Teflon (C) will be compared focusing on CL values.

Figure 4 (see text)

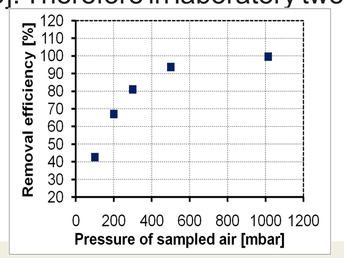


Figure 5 : Calculated removal efficiency of radicals HO_2

HO_2 reaching the amplification zone after time t in the novel reactor has been calculated for different pressures as $(HO_2)_1=(HO_2)_{initial} * exp(-t*k_w)$ (Fig. 4). Previous work [4] has shown that a k_w=1.5 s^{-1} reproduces reasonably the variation of the CL with the pressure (Fig 5). As the mass flow through the reactor is kept constant, the volume flow increases with pressure and the residence time of air decreases and thus less radicals are removed. This is an important consideration for the deployment of PERCA for radical speciation in airborne measurements.

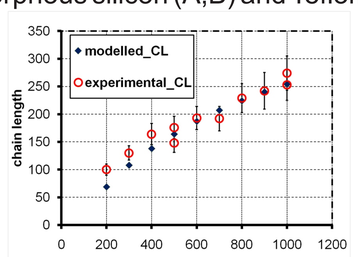


Figure 6 : Experimental and simulated variations of CL =f(P) for k_w=1.5 s^{-1}

References

[1] A new technique for the selective measurement of atmospheric peroxy radical concentrations of HO_2 and RO_2 using a denuding method, K. Miyazaki, A. E. Parker, C. Fittschen, P. S. Monks, and Y. Kajii, Atmos. Meas. Tech., 3, 1547-1554, 2010
[2] Peroxy Radical InterComparison Experiment; Final Report, PRICE 1994, A.Volz-Thomas et.al., 1995.
[3] Laboratory studies of the response of a peroxy radical chemical amplifier to HO_2 and a series of organic peroxy radicals, Ashbourn S., Jenkin M., . Clemitshaw K. Journal of Atmospheric Chemistry 29: 233–266, 1998.
[4] Characterization and optimization of a dual channel PERCA for the investigation of the chemistry of peroxy radicals in the upper troposphere, PhD thesis, Kartal D., University of Bremen, 2009.

Universität Bremen

We acknowledge funding by the DFG Deutsche Forschungsgemeinschaft within the HALO SPP (proposal BU 688/16-1) project REVOLVER

www.iup.uni-bremen.de