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A novel semi-direct method to measure OH reactivity by chemical ionization mass spectrometry (CIMS)

Jennifer B. A. Muller et al.

Correspondence to: Dagmar Kubistin (dagmar.kubistin@dwd.de)

S1. FACSIMILE 0D modelling of chemistry within CIMS flow tube

The following chemical mechanism has been used for the simulations described in the main paper. Only the reactions relevant to the results discussed in the main text are shown in Table S1.

Concentrations and parameters that are initialised for the flow tube experiments:

OH wall loss, HO_2 wall loss, O_2, N_2, H_2O, HO_2, NO, NO_2, CO, OH, H_2SO_4, C_3H_8

All other species are initialised zero.

RO_2 are lumped and represent $RO_2 = IC_3H_7O_2 + NC_3H_7O_2$

Table S1: Reactions in the flow tube relevant to HOx recycling in the CIMS flow tube

Reaction		Rate constant at T = 284 K, p = 995 hPa	Comment
$OH + CO$	$= H + CO_2$	1.1×10^{-13}	
$OH + CO$	$= HOCO$	1.3×10^{-13}	
$HOCO + O_2$	$= HO_2 + CO_2$	2.0×10^{-12}	
$OH + NO_2$	$= HNO_3$	1.4×10^{-11}	
$HO_2 + NO$	$= OH + NO_2$	8.1×10^{-12}	
$HO_2 + NO_2$	$= HO_2NO_2$	1.3×10^{-12}	
$OH + NO$	$= HONO$	8.0×10^{-12}	
$OH + HO_2$	$= H_2O + O_2$	1.1×10^{-10}	
$HO_2 + HO_2$	$= H_2O_2 + O_2$	1.5×10^{-12}	
$SO_2 + OH$	**$= HSO_3$**	1.0×10^{-12}	
$HSO_3 + O_2$	**$= SO_3 + HO_2$**	4.4×10^{-13}	
$SO_2 + HO_2$	$= SO_3 + OH$	1.0×10^{-18}	
$SO_2 + IC_3H_7O_2$	$= SO_3 + IC_3H_7O$	3.5×10^{-17}	*
$SO_2 + NC_3H_7O_2$	$= SO_3 + NC_3H_7O$	3.5×10^{-17}	*
$SO_3 + H_2O + H_2O$	**$= H_2SO_4 + H_2O$**	8.4×10^{-31}	
OH	$= N_2$	$8.2\ s^{-1}$	OH wall loss rate
HO_2	$= N_2$	$0\ s^{-1}$	HO_2 wall loss rate
$OH + C_3H_8$	$= IC_3H_7O_2$	9.8×10^{-13}	branching ratio = 0.736
$OH + C_3H_8$	$= NC_3H_7O_2$	9.8×10^{-13}	branching ratio = 0.264
$IC_3H_7O_2 + NO$	$= IC_3H_7O + NO_2$	9.6×10^{-12}	branching ratio = 0.958
$NC_3H_7O_2 + NO$	$= NC_3H_7O + NO_2$	9.9×10^{-12}	branching ratio = 0.980
IC_3H_7O	$= CH_3COCH_3 + HO_2$	6.7×10^{-15}	k x $[O_2]$
NC_3H_7O	$= C_2H_5CHO + HO_2$	1.1×10^{-14}	k x $[O_2]$
$IC_3H_7O_2 + HO_2$	$= IC_3H_7OOH$	2.8×10^{-11}	k x 0.520
$IC_3H_7O_2 + NO$	$= IC_3H_7NO_3$	9.6×10^{-12}	branching ratio = 0.042
$IC_3H_7O_2$	$= N_2$	3.2×10^{-14}	k x $[RO_2]$
$NC_3H_7O_2 + HO_2$	$= NC_3H_7OOH$	2.8×10^{-11}	k x 0.520
$NC_3H_7O_2 + NO$	$= NC_3H_7NO_3$	9.9×10^{-12}	branching ratio = 0.020
$NC_3H_7O_2$	$= N_2$	6.5×10^{-13}	k x $[RO_2]$

* These rate constants are estimates based on analogy reactions $SO_2 + HO_2$ and $SO_2 + CH_3O_2$. They should be considered uncertain and as an upper limit.

The following reactions are added to those in Table S1 when tagging for recycled OH (OHrec) is used and H_2SO_4 production pathways are separated:

OHrec + CO	=	H + CO_2
OHrec + CO	=	HOCO
OHrec + NO_2	=	HNO_3
HO_2 + NO	=	OHrec + NO_2
OHrec + NO	=	HONO
OHrec + HO_2	=	H_2O + O_2
OHrec + C_3H_8	=	$IC_3H_7O_2$
OHrec + C_3H_8	=	$NC_3H_7O_2$
OHrec	=	N_2
SO_2 + OHrec	=	HSO_3rec
HSO_3rec + O_2	=	SO_3OHrec + HO_2
SO_3OHrec + H_2O +H_2O	=	H_2SO_4OHrec + H_2O
SO_2 + HO_2	=	SO_3HO_2 + OHrec
SO_3HO_2 + H_2O + H_2O	=	$H_2SO_4HO_2$ + H_2O
SO_2 + $IC_3H_7O_2$	=	SO_3RO_2 + IC_3H_7O
SO_2 + $NC_3H_7O_2$	=	SO_3RO_2 + NC_3H_7O
SO_3RO_2 + H_2O +H_2O	=	$H_2SO_4RO_2$ + H_2O

S2. OH kinetic rate constants

Recommended rate constants from both IUPAC (Atkinson et al., 2006) and JPL assessments (Burkholder et al., 2015) are provided with uncertainty factors, which are considered here. Also discrepancies coming from the difference between recommendations are assessed for cases CO and C_3H_8 as OH reactants (Table S2). IUPAC standard temperature of 273.15 K and pressure of 10^5 Pa are used here in the calculations of OH reactivity.

Table S2: Comparison of uncertainties in scaling rate from uncertainties and differences in kinetic rate constants for OH reactants CO and propane

OH reactant	Carbon monoxide (CO)	Propane (C_3H_8)
Reaction(s)	$k = k_1 + k_2$ k_1 : OH + CO → H + CO_2 k_2 : OH + CO + M → HOCO + M	k : OH + C_3H_8 → products
Uncertainty in sr_{CIMS} based on IUPAC rate constant uncertainty (1 sigma)	11 %	5 %
Uncertainty in sr_{CIMS} based on JPL rate constant uncertainty (1 sigma)	12 %	7 %
Difference in means between recommendations	< 4 % *	3 %

* This includes an additional IUPAC recommendation for k directly, valid for T = 200-300 K and p = 0-1 bar N_2

For CO as OH reactant, the 1 sigma uncertainty in the mean scaling rate is 11 % for IUPAC and 12 % for JPL recommendations. The difference in CIMS scaling rates from using the different recommendations is less than 4 % (Table S2), showing that the uncertainties in the rate constants themselves dominate the uncertainty in the scaling rate. Therefore the difference between recommendations is compatible within the uncertainties of the rate constant themselves.

In the case of propane as OH reactant, the 1 sigma uncertainty in the mean scaling rate is 5 % and 7 % for IUPAC and JPL recommendations respectively. The difference in mean calculated OH reactivity for the two recommendations is 3 %. The difference between recommendations is therefore at the order of the 1 sigma uncertainty of the rate constant themselves.

S3. Wall loss rate measurements during OH reactivity comparison campaign at FZJ SAPHIR chamber, April 2016

To provide an additional illustration of the quality of the wall loss measurements, rates from the OH reactivity comparison campaign at the SAPHIR chamber (Fuchs et al., 2017) are shown in Fig. S3. During the campaign in April 2016, zero OH reactivity was measured every day. At the beginning of each day, the chamber was humidified without addition of OH reactants, i.e. zero OH reactivity in the chamber, so consequently the wall loss rates could be obtained for the period of 0.5-1 hour.

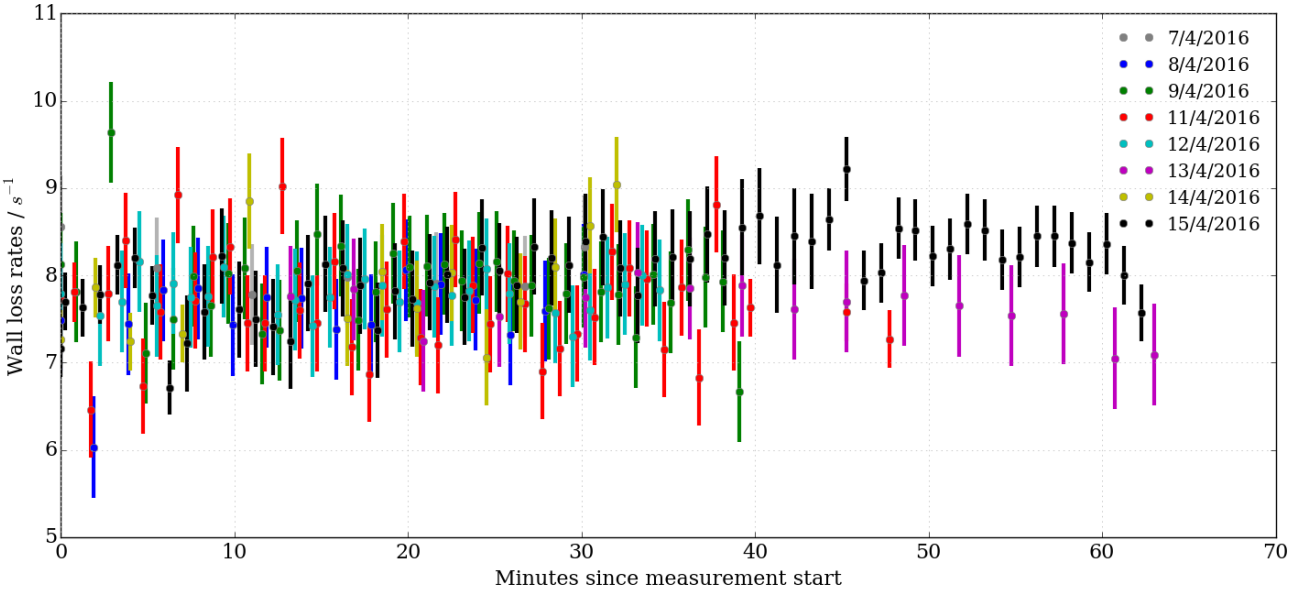

Figure S3. Time series of wall loss rate k_w measurements for periods of zero OH reactivity in the SAPHIR chamber

The wall loss rates are overall stable for each individual day, and also for the whole campaign period from 7th to 15th April 2016.

Looking at stability over longer periods of time (half a year), the CIMS wall loss rates in Table 2 give indication of a similar level of variability and uncertainty compared to the shorter term stability shown above.