

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, HO₂ wall loss, O₂, N₂, H₂O, HO₂, NO, NO₂, CO, OH, H₂SO₄, C₃H₈

All other species are initialised zero.

RO₂ are lumped and represent RO₂ = IC₃H₇O₂ + NC₃H₇O₂

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

Reaction	Rate constant at T = 284 K, p = 995 hPa	Comment
OH + CO = H + CO ₂	1.1 x 10 ⁻¹³	
OH + CO = HOCO	1.3 x 10 ⁻¹³	
HOCO + O ₂ = HO ₂ + CO ₂	2.0 x 10 ⁻¹²	
OH + NO ₂ = HNO ₃	1.4 x 10 ⁻¹¹	
HO ₂ + NO = OH + NO ₂	8.1 x 10 ⁻¹²	
HO ₂ + NO ₂ = HO ₂ NO ₂	1.3 x 10 ⁻¹²	
OH + NO = HONO	8.0 x 10 ⁻¹²	
OH + HO ₂ = H ₂ O + O ₂	1.1 x 10 ⁻¹⁰	
HO ₂ + HO ₂ = H ₂ O ₂ + O ₂	1.5 x 10 ⁻¹²	
SO₂ + OH = HSO₃	1.0 x 10 ⁻¹²	
HSO₃ + O₂ = SO₃ + HO₂	4.4 x 10 ⁻¹³	
SO ₂ + HO ₂ = SO ₃ + OH	1.0 x 10 ⁻¹⁸	
SO ₂ + IC ₃ H ₇ O ₂ = SO ₃ + IC ₃ H ₇ O	3.5 x 10 ⁻¹⁷	*
SO ₂ + NC ₃ H ₇ O ₂ = SO ₃ + NC ₃ H ₇ O	3.5 x 10 ⁻¹⁷	*
SO₃ + H₂O + H₂O = H₂SO₄ + H₂O	8.4 x 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 ₃ H ₈ = IC ₃ H ₇ O ₂	9.8 x 10 ⁻¹³	branching ratio = 0.736
OH + C ₃ H ₈ = NC ₃ H ₇ O ₂	9.8 x 10 ⁻¹³	branching ratio = 0.264
IC ₃ H ₇ O ₂ + NO = IC ₃ H ₇ O + NO ₂	9.6 x 10 ⁻¹²	branching ratio = 0.958
NC ₃ H ₇ O ₂ + NO = NC ₃ H ₇ O + NO ₂	9.9 x 10 ⁻¹²	branching ratio = 0.980
IC ₃ H ₇ O = CH ₃ COCH ₃ + HO ₂	6.7 x 10 ⁻¹⁵	k x [O ₂]
NC ₃ H ₇ O = C ₂ H ₅ CHO + HO ₂	1.1 x 10 ⁻¹⁴	k x [O ₂]
IC ₃ H ₇ O ₂ + HO ₂ = IC ₃ H ₇ OOH	2.8 x 10 ⁻¹¹	k x 0.520
IC ₃ H ₇ O ₂ + NO = IC ₃ H ₇ NO ₃	9.6 x 10 ⁻¹²	branching ratio = 0.042
IC ₃ H ₇ O ₂ = N ₂	3.2 x 10 ⁻¹⁴	k x [RO ₂]
NC ₃ H ₇ O ₂ + HO ₂ = NC ₃ H ₇ OOH	2.8 x 10 ⁻¹¹	k x 0.520
NC ₃ H ₇ O ₂ + NO = NC ₃ H ₇ NO ₃	9.9 x 10 ⁻¹²	branching ratio = 0.020
NC ₃ H ₇ O ₂ = N ₂	6.5 x 10 ⁻¹³	k x [RO ₂]

* These rate constants are estimates based on analogy reactions SO₂ + HO₂ and SO₂ + CH₃O₂. They should be considered uncertain and as an upper limit.

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 C₃H₈ as OH reactants (Table S2). IUPAC standard temperature of 273.15 K and pressure of 10⁵ 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 ₃ H ₈)
Reaction(s)	$k = k_1 + k_2$ $k_1 : \text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ $k_2 : \text{OH} + \text{CO} + \text{M} \rightarrow \text{HOCO} + \text{M}$	$k : \text{OH} + \text{C}_3\text{H}_8 \rightarrow \text{products}$
Uncertainty in sr_{CIMS} based on IUPAC rate constant uncertainty (1 sigma)	15 %	2 %
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 N₂

For CO as OH reactant, the 1 sigma uncertainty in the mean scaling rate is 15 % 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 2 % 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.