

Deliverable D2.4: Report on auxiliary mechanisms with respect to photo-oxidation processes for each chamber

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1. Auxiliary Mechanisms for each chambers

Chamber specific auxiliary chemical mechanisms, taking into account the results of characterization experiments described above, are given below for each chamber. These parameters can be dependent to some extent on previous experiments performed in the chamber, particularly for smaller chambers, and hence regular characterization is carried out, for example at the start of experimental campaigns. These auxiliary mechanisms will be transferred to The Database of Atmospheric Simulation Chamber Studies (DASCS) to facilitate their use in conjunction with the experimental data stored on the database.

1.1. Auxiliary mechanism determined from SAPHIR (Rohrer et al., 2005)

Parameter	Rate	Experiment
Dilution	$X + \text{DIL} \rightarrow$ $k = \text{flow}$	flow from flow controller monitoring
OH background reactivity	$Y + \text{OH} \rightarrow \text{HO}_2$ e.g. $k_{\text{CO}+\text{OH}}$ Typical $k = 1 - 2 \text{ s}^{-1}$	Y determined in each experiment by $k(\text{OH})$ in the clean chamber (after humidification)
Photolytic HONO source	$\text{SHONO} \rightarrow \text{HONO}$ $k = S \times 4.7 \times 10^{13} (1 + \text{RH}/11.6)^2 \exp(-3950/T) \cdot j(\text{NO}_2)$	S determined in reference experiments or zero air phase from HONO increase
Photolytic HCHO source	$\text{SHCHO} \rightarrow \text{HCHO}$ $k = S \times 1.9 \times 10^{13} (0.21 + 0.026 \text{ RH}) \exp(-2876/T) \cdot j(\text{NO}_2)$	S determined in reference experiments or zero air phase from HCHO increase
O₃ loss	$\text{O}_3 \rightarrow$ $k = (90 \times 3600)^{-1} \text{ s}^{-1}$	Determined in reference experiments
Other losses		To be determined in reference experiments

1.2. Auxiliary mechanism determined from FORTH

Parameter	Rate (lower - upper limit)	Experiment
O ₃ loss	O ₃ → wO ₃ k = 1 (0.5 – 1.6)	Determined in reference experiments
NO loss	NO → wNO k = 2.5 (2.2 – 3.1) × 10 ⁻⁶ s ⁻¹	Determined in reference experiments
NO ₂ loss	NO ₂ → wNO ₂ k = 0.81 (0.56 – 0.94) × 10 ⁻⁶ s ⁻¹	Determined in reference experiments
Toluene loss	Tol → wTol k = 1.8 (1.2 – 2.1) × 10 ⁻⁶ s ⁻¹	Determined in reference experiments
A-pinene loss	a-pin → w a-pin k = 6 (3.4 – 7.8) × 10 ⁻⁶ s ⁻¹	Determined in reference experiments

1.3. Auxiliary mechanism determined from ILMARI

Parameter	Rate (lower - upper limit)	Experiment
Dilution	$X + \text{DIL} \rightarrow$	The ILMARI chamber is used as a batch reactor. In typical experiments the sample in the chamber is not diluted.
O ₃ loss	$\text{O}_3 \rightarrow \text{wO}_3$ $k = 0.65 (0.5 - 0.8) \times 10^{-6} \text{ s}^{-1}$	Determined in reference experiments
Heterogeneous NO ₂ reaction	$\text{NO}_2 \rightarrow 0.5\text{HONO} + 0.5\text{HNO}_3$ $k = 0.3 (0.2-0.4) \times 10^{-6} \text{ s}^{-1}$ (dry) (up to $4.5 \times 10^{-6} \text{ s}^{-1}$ in humid conditions)	Direct measurement of NO ₂ loss and HONO increase
Photolytic HONO wall source	$h\nu + \text{wall} \rightarrow \text{HONO}$ $k = 3 (1.5-6) \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$	Direct measurement of HONO and comparison to the simulated HONO
Photolytic Heterogeneous NO ₂ reaction	$\text{NO}_2 + h\nu + \text{wall} \rightarrow \text{HONO}$ $k = 9 (4 - 16) \times 10^{-6} \text{ s}^{-1}$	Comparison of simulation and measurements

1.4. Auxiliary mechanism determined from EUPHORE

Parameter	Rate (lower - upper limit)	Experiment
HCOOH wall source	$S \rightarrow \text{HCOOH}$ Light: $k_{\text{dry}} = 2.126 \times 10^{-4} \text{ ppb s}^{-1}$ $k_{50\% \text{ RH}} = 6.617 \times 10^{-4} \text{ ppb s}^{-1}$ Dark: $k_{\text{dry}} = \text{BDL}^a$ $k_{50\% \text{ RH}} = 5.716 \times 10^{-4} \text{ ppb s}^{-1}$	Determined in reference experiments
HCHO wall source	$S \rightarrow \text{HCHO}$ $W(\text{HCHO}) = c \times j(\text{NO}_2) \exp(-T_0/T)$ for ($c = 3.1 \times 10^{17} \text{ cm}^{-3}$ and $T_0 = 5686 \text{ K}$) Light: $k_{\text{dry}} = 1.885 \times 10^{-4} \text{ ppb s}^{-1}$ $k_{50\% \text{ RH}} = 1.366 \times 10^{-4} \text{ ppb s}^{-1}$ Dark: $k_{\text{dry}} = \text{BDL}$ $k_{50\% \text{ RH}} = 0.6883 \times 10^{-4} \text{ ppb s}^{-1}$	Determined in reference experiments Zador et al. (2006)
HONO wall source	$S \rightarrow \text{HONO}$ Dark: $k_{50\% \text{ RH}} = 0.2029 \times 10^{-4} \text{ ppb s}^{-1}$ $W(\text{HONO}) = a \times j(\text{NO}_2) \times \exp(-T_0/T)$ for ($\text{RH} < 2\%$, $a = 7.3 \times 10^{21} \text{ cm}^{-3}$, $T_0 = 8945 \text{ K}$) $W(\text{HONO}) = W(\text{HONO})_{\text{dry}} + j(\text{NO}_2) \times b \times \text{RH}_q$ being ($2\% < \text{RH} < 15\%$, $b = 5.8 \times 10^8 \text{ cm}^{-3}$ and $q = 0.36$)	Determined in reference experiments Zador et al. (2006)
O₃ wall source	$S \rightarrow \text{O}_3$ Light: $k_{\text{dry}} = \text{BDL}$ $k_{50\% \text{ RH}} = 1.574 \times 10^{-4} \text{ ppb s}^{-1}$ Dark: $k_{\text{dry}} = \text{BDL}$ $k_{50\% \text{ RH}} = \text{BDL}$	Determined in reference experiments
NO wall source	$S \rightarrow \text{NO}$ Light: $k_{\text{dry}} = 0.282 \times 10^{-4} \text{ ppb s}^{-1}$ $k_{50\% \text{ RH}} = 2.44 \times 10^{-4} \text{ ppb s}^{-1}$ Dark: $k_{\text{dry}} = 0.699 \times 10^{-4} \text{ ppb s}^{-1}$ $k_{50\% \text{ RH}} = 0.757 \times 10^{-4} \text{ ppb s}^{-1}$	Determined in reference experiments
NO₂ wall source	$S \rightarrow \text{O}_3$ Light: $k_{\text{dry}} = \text{BDL}$ $k_{50\% \text{ RH}} = \text{BDL}$ Dark: $k_{\text{dry}} = \text{BDL}$ $k_{50\% \text{ RH}} = \text{BDL}$	Determined in reference experiments
O₃, NO, NO₂ loss	$X \rightarrow wX$	Dilution is dominant loss term.

^a Below detection limit

1.5. Auxiliary mechanism determined from CSA

Parameter	Rate (lower - upper limit)	Experiment
Wall loss		
O ₃ loss	O ₃ → wO ₃ $k = 2 (1.8 - 35)$	Determined in reference experiments Highly dependent on wall cleaning
NO ₂ loss	NO ₂ → wNO ₂ $k = 1.3 (1 - 2) \times 10^{-4} \text{ s}^{-1}$	Determined in reference experiments
Wall sources		
Heterogeneous NO ₂ reaction	NO ₂ → δHONO + γHNO ₃ $k = 1 (0.1 - 10) \times 10^{-2} \text{ s}^{-1}$	Determined in reference experiments δ = 0.6, γ = 0.1
Photolytic NO ₂ wall source	hν + wall → NO ₂ $k = 1.3 (1 - 2) \times 10^{-4} \text{ ppb s}^{-1}$	Determined in reference experiments
Photolytic HCHO wall source	hν + wall → HCHO $k = 5.5 (5 - 10) \times 10^{-4} \text{ s}^{-1}$	Determined in reference experiments

1.6. Auxiliary mechanism determined for dry conditions from CESAM (Wang et al., 2011)

Parameter	Rate (standard deviation)	Experiment
Wall loss		
NO ₂ loss	NO ₂ → wNO ₂ k = 1.76 (1.66) × 10 ⁻⁴ s ⁻¹	Determined in reference experiments
O ₃ loss	O ₃ → wO ₃ k = 2.33 (0.94) × 10 ⁻⁴ s ⁻¹	Determined in reference experiments Highly dependent on wall cleaning
VOC wall loss		
Carboxylic acid	k = < 1 × 10 ⁻⁶ s ⁻¹	Ethylbutyric acid; T = 295K; RH = 42-52%
Alkene	Propene: k = < 1 × 10 ⁻⁶ s ⁻¹ A-pinene: k = < 1 × 10 ⁻⁶ s ⁻¹ Isoprene: k = 2 (± 1) × 10 ⁻⁶ s ⁻¹	RH < 1 %; T ~ 295 K
Carbonyl	Formaldehyde: k = < 10 × 10 ⁻⁶ s ⁻¹ Hexanal: k = 70 (± 30) × 10 ⁻⁶ s ⁻¹	RH < 1 %; T ~ 295 K RH = 42-52% ; T ~ 295 K
Aromatic	Methylstyrene: k = 3 (± 0.5) × 10 ⁻⁶ s ⁻¹	RH < 1 %; T ~ 295 K
Carbonyl nitrate	Nitroxyacetone: k = 5 (± 2) × 10 ⁻⁶ s ⁻¹	RH < 1 %; T ~ 295 K
Wall sources		
Photolytic	NO ₂ + hv → δHONO + γHNO ₃	Determined in reference experiments
Heterogeneous NO ₂ reaction	k = 1.11 (0.55) × 10 ⁻³ s ⁻¹	δ = 0.5, γ = 0.1 (with j(NO ₂) = 0.003)
Heterogeneous NO ₂ reaction	NO ₂ → αHONO + βHNO ₃ k = 3.08 (2.92) × 10 ⁻² s ⁻¹	Determined in reference experiments α = 0.3, β = 0.07

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1.7. Auxiliary mechanism determined from HIRAC (Glowacki et al., 2008; Onel et al., 2017)

Parameter	Rate	Experiment
Dilution	$X + \text{DIL} \rightarrow$ Typical $k = 4 \times 10^{-5} \text{ s}^{-1}$	flow from flow controller monitoring
Wall loss		
$\text{O}_3, \text{NO}, \text{NO}_2$ loss	$X \rightarrow wX$ Typical $k \leq 1 \times 10^{-5} \text{ s}^{-1}$	Determined in reference experiments Highly dependent on wall cleaning and previous experiments
VOC loss	$\text{VOC} \rightarrow \text{loss}$	Monitored in real time via GC or FTIR. Dilution is often dominant loss term.
HO_2 loss	$\text{HO}_2 \rightarrow \text{loss}$	Determined from HO_2 mixed order decays (see Figure 8, Glowacki et al. (2008))
Wall sources		
HOx production	$h\nu \rightarrow \text{HOx}$ Minor	FAGE used to monitor HOx production in synthetic air with lights on.

1.8. Auxiliary mechanism determined from PACS-C3 (Paulsen et al. 2005; Metzger et al., 2008)

Parameter	Rate (lower - upper limit)	Experiment
Dilution	$X + \text{DIL} \rightarrow$	flow from flow controller monitoring
Initial HONO concentration	$[\text{HONO}]_0 = 0.074 \times \text{RH} + 0.006 \times [\text{NO}_2]$ Typical $[\text{HONO}]_0 = 0 - 3$ ppb	Determined in reference experiments
Heterogeneous NO₂ reaction	$\text{NO}_2 \rightarrow 0.5\text{HONO} + 0.5\text{HNO}_3$ $k = 0.53 (0.21 - 4.2) \times 10^{-6} \text{ s}^{-1}$	Determined in reference experiments
N₂O₅	$\text{N}_2\text{O}_5 \rightarrow 2\text{wHNO}_3$ $k = 1 (0.5 - 4.7) \times 10^{-5} \text{ s}^{-1}$	Adopted from Carter and Lurmann (1991), and Bloss et al. (2005)
N₂O₅ hydrolysis	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{wHNO}_3$ $k = 1 (0.0011 - 13) \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$	
Background OH reactivity	$\text{OH} + \text{X} \rightarrow \text{HO}_2 + \text{X}$ $k = k_{\text{CO}+\text{OH}}$ Typical $X_0 = 300 (100-600)$ ppb	
Wall loss		
O ₃ loss	$\text{O}_3 \rightarrow \text{wO}_3$ $k = 4 (2 - 8) \times 10^{-6} \text{ s}^{-1}$	Determined in reference experiments
HNO ₃ loss	$\text{HNO}_3 \rightarrow \text{wHNO}_3$ $k = 1 (0.5 - 2) \text{ s}^{-1}$	Adopted from Bloss et al. (2005)
Wall HNO ₃ photolysis	$\text{wHNO}_3 + h\nu \rightarrow \text{NO}_2 + \text{OH}$ $j_{\text{HNO}_3} (0 - 2 j_{\text{HNO}_3})$	
Wall sources		
Photolytic HONO source	$\text{SHONO} \rightarrow \text{HONO}$ $k = 9.1 (5 - 13) \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$	Determined in reference experiments
Photolytic HCHO source	$\text{SHCHO} \rightarrow \text{HCHO}$ $k = 5 (2.5 - 10) \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$	Determined in reference experiments

1.9. Auxiliary mechanism determined from UMAN-MAC

Parameter	Rate	Experiment
Dilution	$X + \text{DIL} \rightarrow$	MAC is run as a batch reactor. In typical experiments, no dilution is applied.
Wall loss		
O ₃ loss	$\text{O}_3 \rightarrow \text{wO}_3$ $k = 1.08 \times 10^{-6} \text{ s}^{-1}$	Determined in reference experiments
NO ₂ loss	$\text{NO}_2 \rightarrow \text{wNO}_2$ $k = 1.34 \times 10^{-6} \text{ s}^{-1}$	Determined in reference experiments
Toluene loss	$\text{Tol} \rightarrow \text{wTol}$ $k = 2.12 \times 10^{-7} \text{ s}^{-1}$	Determined in reference experiments
α -pinene loss	$\text{a-pin} \rightarrow \text{w a-pin}$ $k = 1.97 \times 10^{-7} \text{ s}^{-1}$	Determined in reference experiments
1,3,5-TMB	$\text{TMB} \rightarrow \text{wTMB}$ $k = 2.45 \times 10^{-7} \text{ s}^{-1}$	Determined in reference experiments

1.10. References

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