

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 |

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 | | |
| O₃ loss | $\text{O}_3 \rightarrow \text{wO}_3$ $k = 4 (2 - 8) \times 10^{-6} \text{ s}^{-1}$ | Determined in reference experiments |
| HNO₃ loss | $\text{HNO}_3 \rightarrow \text{wHNO}_3$ $k = 1 (0.5 - 2) \text{ s}^{-1}$ | Adopted from Bloss et al. (2005) |
| Wall HNO₃ 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.

1.10. 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 |

1.11. References

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