

# Electronic supplementary information to “Heterogeneous OH oxidation of biomass burning organic aerosol surrogate compounds: Assessment of volatilisation products and the role of OH concentration on the reactive uptake kinetics”

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## 1 Box model description

OH concentrations applied in the atmospheric pressure flow reactor were quantified using a photochemical box model based on 24 O<sub>x</sub> and HO<sub>x</sub> cycling/self reactions<sup>1</sup> and the photolysis of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> as shown in Table S1. This model includes heterogeneous loss to halocarbon wax for several of the reactive species including OH, O, and HO<sub>2</sub>. The output of this model is shown in Fig. S1. We measured the uptake of OH by halocarbon wax at similar [OH] ( $\sim 10^{10}$  molecule cm<sup>-3</sup>) as applied in the atmospheric pressure flow reactor ([OH]  $\sim 2 \times 10^{10}$  molecule cm<sup>-3</sup>) and observed an average  $\gamma = 8 \times 10^{-4}$ . The reactive uptake of O and HO<sub>2</sub> by halocarbon wax as far as we know has not been reported in the literature. We assume that  $\gamma$  for O and HO<sub>2</sub> are similar to  $\gamma$  for OH uptake by halocarbon wax.  $\gamma$  for O<sub>3</sub> uptake by halocarbon wax was at or below our detection limit of  $\gamma \leq 10^{-6}$ , so we apply  $\gamma$  for O<sub>3</sub> uptake by halocarbon wax as  $10^{-6}$ . The photolysis rate of O<sub>3</sub> using the UV lamp was estimated based on loss measurements of [O<sub>3</sub>] under O<sub>3</sub>/O<sub>2</sub> flow using an ozone monitor. Based on these loss measurements over a range of [O<sub>3</sub>] we determined an average photolysis rate

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of  $\sim 0.042 \text{ s}^{-1}$ . The box model shows the evolution of the different oxidants potentially forming during the production of OH. The largest concentrations are that of  $\text{H}_2\text{O}$  (black), held near 60% RH, and  $\text{O}_2$  (red), and do not change significantly over time. For all of the other species in Fig. S1, steady-state is reached on the order of milliseconds except for  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$  that continue to build-up over time. OH (yellow) reaches steady-state in about 0.1 seconds, but begins to decrease due to gas-phase reactions with other species as well as heterogeneous loss to the halocarbon wax coated walls of the flow reactor.  $\text{O}_3$  concentrations were maintained near 12 ppm during volatilisation measurements resulting in  $\sim 0.8$  ppb OH according to the box model. In a set of separate experiments, a known trace quantity of isoprene was added to the flow and based on the reaction rate of isoprene with OH ( $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ )<sup>1</sup> [OH] was determined over a range of initial [ $\text{O}_3$ ] ( $\sim 500$  ppb–15 ppm) as shown in Fig. S2. Within experimental uncertainties based on the error in the reaction rate constant of isoprene and OH, our photochemical box model is in good agreement with the measured values over a range of initial [ $\text{O}_3$ ].

## 2 HR-PTR-ToF-MS sampling protocol and signal analysis

The HR-PTR-ToF-MS experiments were run for 600 sec resulting in 600 scans per experiment. In the case of OH impacted experiments, the background signal (in the presence of both  $\text{H}_2\text{O}$  vapour and  $\text{O}_3$ ) was recorded for  $\sim 250$  scans at which point the UV lamp was switched on to allow for OH production. We continued to record the signal in the presence of OH for an additional 950 scans, where the last experimental run period of 600 scans (600 sec) was taken as the average signal in the presence of OH. Prior to switching on the UV lamps, the impacts of background ( $\text{N}_2/\text{O}_2$  alone,  $\text{N}_2/\text{O}_2/\text{H}_2\text{O}$ ,  $\text{N}_2/\text{H}_2\text{O}/\text{O}_3/\text{O}_2$ , and  $\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{UV}$ ) both in the presence and absence of the organic substrate were assessed using the same sampling protocol. Because the HR-PTR-ToF-MS has a high sampling rate and mass resolution, the peaks were first quantified by integrating over a pre-defined mass-corrected protonated  $m/z$  range, based on well defined signals at  $\text{H}_3^{18}\text{O}^+$  ( $m/z=21.0221$  Th),  $\text{NO}^+$  ( $m/z=29.9979$  Th), and acetone( $\text{H}^+$ ) ( $m/z=59.049$  Th), using PTR-MS ToF viewer 1.4 software. Mass calibration was done prior to sampling as well, so there was little mass shift correction post sampling. The pre-defined mass ranges used for integration of the major peaks discussed here were held constant between background experiments and experiments in the presence

of the organic substrate and OH as to not artificially increase or decrease the integrated intensities between the two experiments.

## References

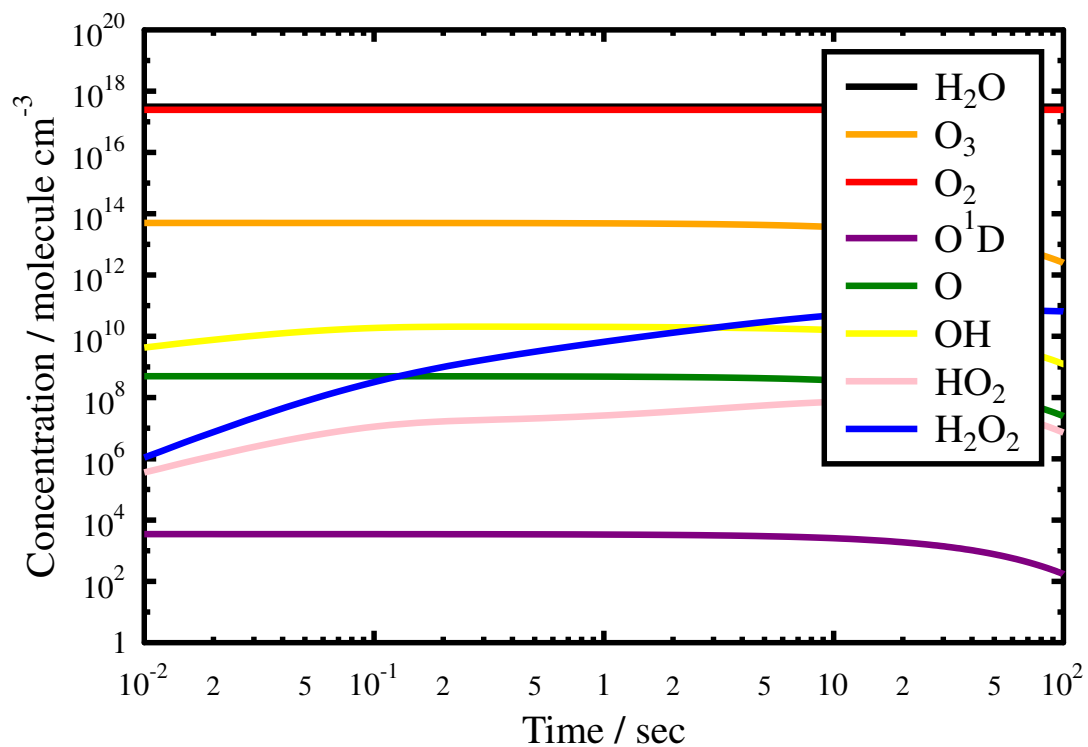
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### 3 Tables

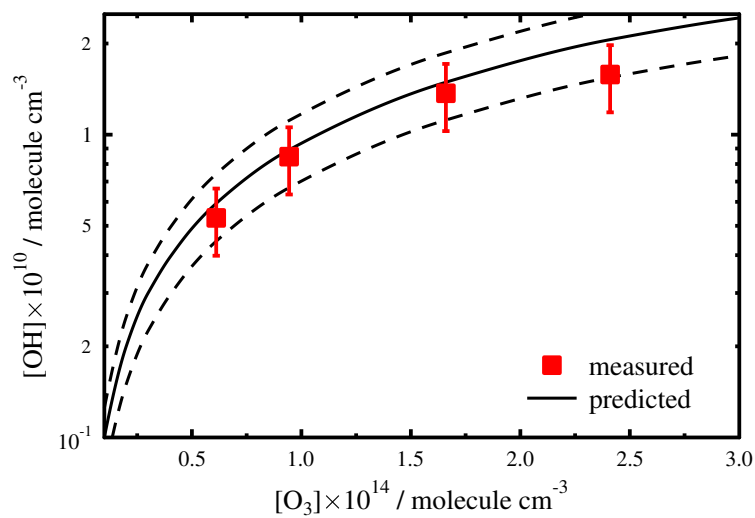
**Table 1** Reactions for photochemical box model

R1	+	R2	→	P1	+	P2	<i>j, k, and γ</i>
O <sub>3</sub>	+	<i>hν</i>		O <sup>1</sup> D	+	O <sub>2</sub>	<i>j</i> = 0.042 s <sup>-1</sup>
O <sup>1</sup> D	+	M		O	+	M	2E-11 cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
O <sup>1</sup> D	+	H <sub>2</sub> O		OH	+	OH	2.2E-10 cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
O <sup>1</sup> D	+	H <sub>2</sub>		OH	+	H	1.1E-10 cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
O	+	OH		O <sub>2</sub>	+	H	2.4E-11e <sup>(<math>\frac{110}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
H	+	O <sub>2</sub>		HO <sub>2</sub>			5.4E-32 cm <sup>6</sup> molecule <sup>-2</sup> sec <sup>-1</sup>
H	+	HO <sub>2</sub>		2OH			8E-11 cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
H	+	HO <sub>2</sub>		H <sub>2</sub>	+	O <sub>2</sub>	5.6E-12 cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
H	+	HO <sub>2</sub>		H <sub>2</sub> O	+	O	2.4E-12 cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
O	+	HO <sub>2</sub>		OH	+	O <sub>2</sub>	2.7E-11e <sup>(<math>\frac{224}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
OH	+	OH		H <sub>2</sub> O	+	O	6.2E-14( $\frac{T}{298}$ ) <sup>2.6</sup> e <sup>(<math>\frac{945}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
OH	+	OH		H <sub>2</sub> O <sub>2</sub>			6.9E-31( $\frac{T}{300}$ ) <sup>-0.8</sup> cm <sup>6</sup> molecule <sup>-2</sup> sec <sup>-1</sup>
O <sup>1</sup> D	+	O <sub>3</sub>		O <sub>2</sub>	+	O	2.4E-10 cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
H	+	O <sub>3</sub>		OH	+	O <sub>2</sub>	2.9E-11 cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
OH	+	O <sub>3</sub>		HO <sub>2</sub>	+	O <sub>2</sub>	1.7E-12e <sup>(<math>\frac{-940}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
OH	+	HO <sub>2</sub>		H <sub>2</sub> O	+	O <sub>2</sub>	4.8E-11e <sup>(<math>\frac{250}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
HO <sub>2</sub>	+	O <sub>3</sub>		OH	+	2O <sub>2</sub>	2.03E-16( $\frac{T}{300}$ ) <sup>4.57</sup> e <sup>(<math>\frac{693}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
HO <sub>2</sub>	+	HO <sub>2</sub>		H <sub>2</sub> O <sub>2</sub>	+	O <sub>2</sub>	2.2E-13e <sup>(<math>\frac{600}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
OH	+	H <sub>2</sub> O <sub>2</sub>		H <sub>2</sub> O	+	HO <sub>2</sub>	2.9E-12e <sup>(<math>\frac{-160}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
O	+	H <sub>2</sub> O <sub>2</sub>		OH	+	HO <sub>2</sub>	1.4E-12e <sup>(<math>\frac{-2000}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
O	+	O <sub>3</sub>		2O <sub>2</sub>			8E-12e <sup>(<math>\frac{-2060}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
O <sup>1</sup> D	+	O <sub>2</sub>		O	+	O <sub>2</sub>	3.2E-11e <sup>(<math>\frac{67}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
OH	+	wall		loss			<i>γ</i> = 8E-4
O	+	wall		loss			<i>γ</i> ≈ 8E-4
HO <sub>2</sub>	+	wall		loss			<i>γ</i> ≈ 8E-4
O <sub>3</sub>	+	wall		loss			<i>γ</i> ≈ 1E-6
OH	+	H <sub>2</sub>		H <sub>2</sub> O	+	H	7.7E-12e <sup>(<math>\frac{-2100}{T}</math>)</sup> cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
O	+	O <sub>2</sub>		O <sub>3</sub>			5.6E-34( $\frac{T}{300}$ ) <sup>-2.6</sup> cm <sup>6</sup> molecule <sup>-2</sup> sec <sup>-1</sup>
H <sub>2</sub> O <sub>2</sub>	+	<i>hν</i>		2OH			<i>j</i> ≈ 1E-5 s <sup>-1</sup>

## 4 Graphics



**Fig. 1** Atmospheric pressure flow reactor box model of gas-phase concentrations due to the production of OH from O<sub>3</sub> photolysis in the presence of O<sub>2</sub> and H<sub>2</sub>O.



**Fig. 2** OH predicted by the photochemical box model (line) compared to measured [OH] derived from isoprene + OH loss experiments (squares). Error bars and dashed lines represent  $\pm 25\%$  uncertainty in the rate constant of OH and isoprene.