

# Supporting Information for “Halogen activation and radical cycling initiated by imidazole-2-carboxaldehyde photochemistry”

Pablo Corral Arroyo<sup>1,2</sup>, Raffael Aellig<sup>3</sup>, Peter A. Alpert<sup>1</sup>, Rainer Volkamer<sup>4,5</sup>, Markus Ammann<sup>1\*</sup>

<sup>1</sup> Paul Scherrer Institute, Laboratory of Environmental Chemistry, 5232 Villigen PSI, Switzerland.

<sup>2</sup> Department of Chemistry and Biochemistry, University of Bern, 2012 Bern, Switzerland.

<sup>3</sup> ETH Swiss Federal Institute of Technology Zürich, Institute for Atmospheric and Climate Science, 8006, Zurich, Switzerland.

<sup>4</sup> Department of Chemistry and Biochemistry, 215 UCB, University of Colorado, Boulder, CO 80309, USA

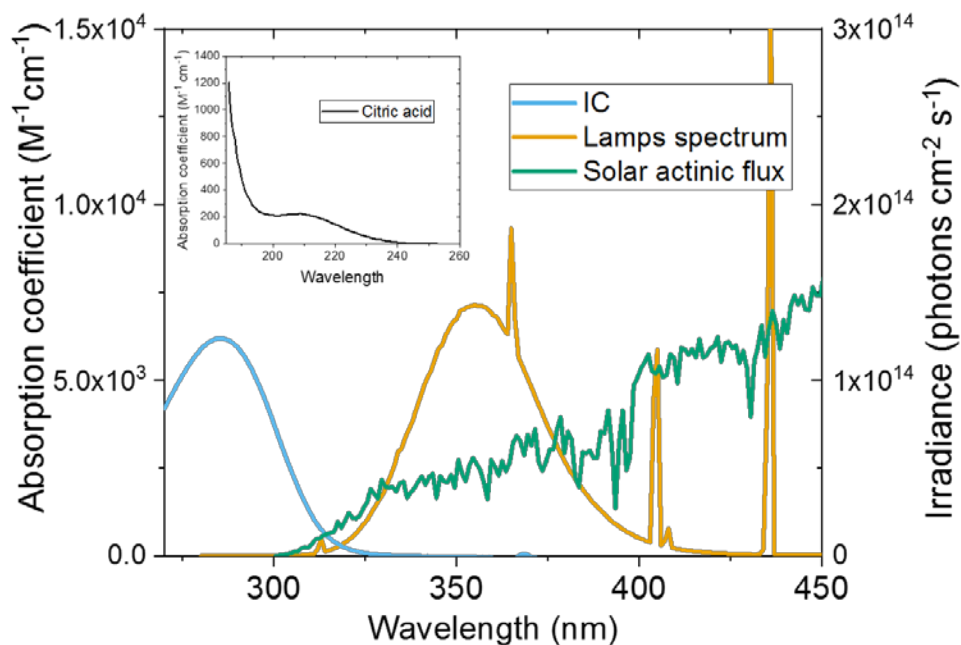
<sup>5</sup> Cooperative Institute for Research in Environmental Sciences (CIRES), 216 UCB, University of Colorado, Boulder, CO 80309, USA

\*[markus.ammann@psi.ch](mailto:markus.ammann@psi.ch) Ph: +41 56 310 4049, Paul Scherrer Institute

In total 10 pages, 4 figures and 1 tables.

## 1. Spectra

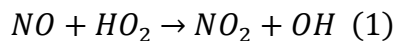
The absorption spectra for imidazole-2-carboxaldehyde (IC) and citric acid (CA) are shown together with the irradiance of the lamps used and the solar irradiance for the surface of the Earth at 48° zenith angle (Figure S1). The overlap between the absorption spectra of IC and the lamps spectrum is orders of magnitude higher than the overlap between the absorption spectra of CA and the lamps spectrum. This corroborates that IC is the primary chromophore in the system.



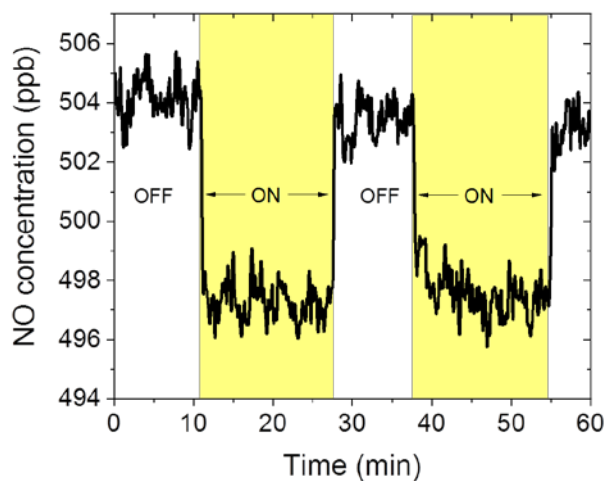
**Figure S1.** Absorption spectra of IC (100 mM) and CA (from NIST Chemistry WebBook), irradiance spectrum of the UV lamps used and solar irradiance at 48° zenith angle.

## 2. NO loss and conversion to HO<sub>2</sub> production

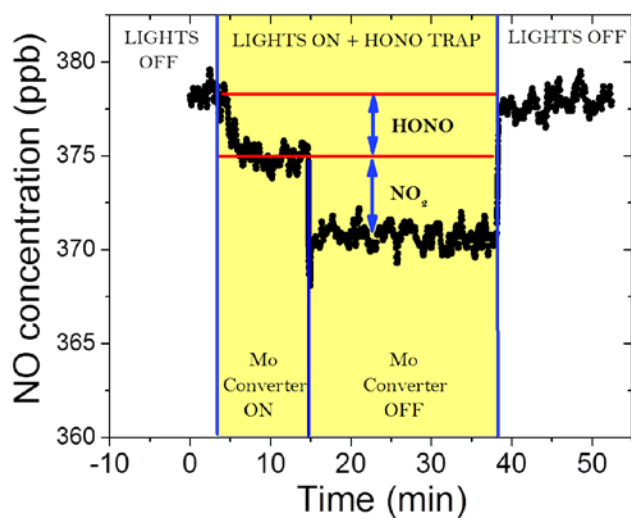
NO was added to the gas flow in sufficient excess so that it acts as the scavenger for HO<sub>2</sub>. A clear NO loss is detected upon switching on UV lights (Fig. S2) due to the release of HO<sub>2</sub> radicals into the gas phase and reaction of NO with HO<sub>2</sub> to form NO<sub>2</sub> and OH radical. OH is scavenged by NO to produce HONO. The chemiluminescence detector was preceded by a HONO trap with an optional bypass, and a molybdenum converter kept at 360°C, also with an optional bypass, to convert HONO and NO<sub>2</sub> into NO. This configuration allowed determining NO, NO<sub>2</sub> and HONO independently by differential measurements (Fig. S2 and S3). As in previous experiments (González Palacios et al., 2016), the ratio NO<sub>2</sub>/HONO was about 1.4. The presence of HONO confirms that HO<sub>2</sub> was indeed the oxidant of NO, rather than another RO<sub>2</sub> species. The fact that the ratio to NO<sub>2</sub> is less than one indicates that some of the OH radicals may be lost at the surface in spite of the large NO concentration or that some HONO may decompose heterogeneously over the film or along tubing downstream of the CWFT. NO was added with a third flow of 5-10 ml/min of 100ppm NO in N<sub>2</sub>. The NO concentration during CWFT experiments was always in excess of 10<sup>13</sup> molecule cm<sup>-3</sup> to efficiently scavenge 99% of HO<sub>2</sub> produced by the films within at most 50 ms ( $k_1 = 8.0 \cdot 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K (Atkinson et al., 2004);  $t_{99\%} = \frac{-\ln(0.01)}{k_1[NO]}$ ).



The reaction between OH and iodine ( $k = 2.1 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) can interfere with the reaction between OH and NO just at high concentrations of iodide (>0.001 M) when the iodine concentration may reach levels of 10<sup>11</sup> - 5 × 10<sup>12</sup> molecules cm<sup>-3</sup>.



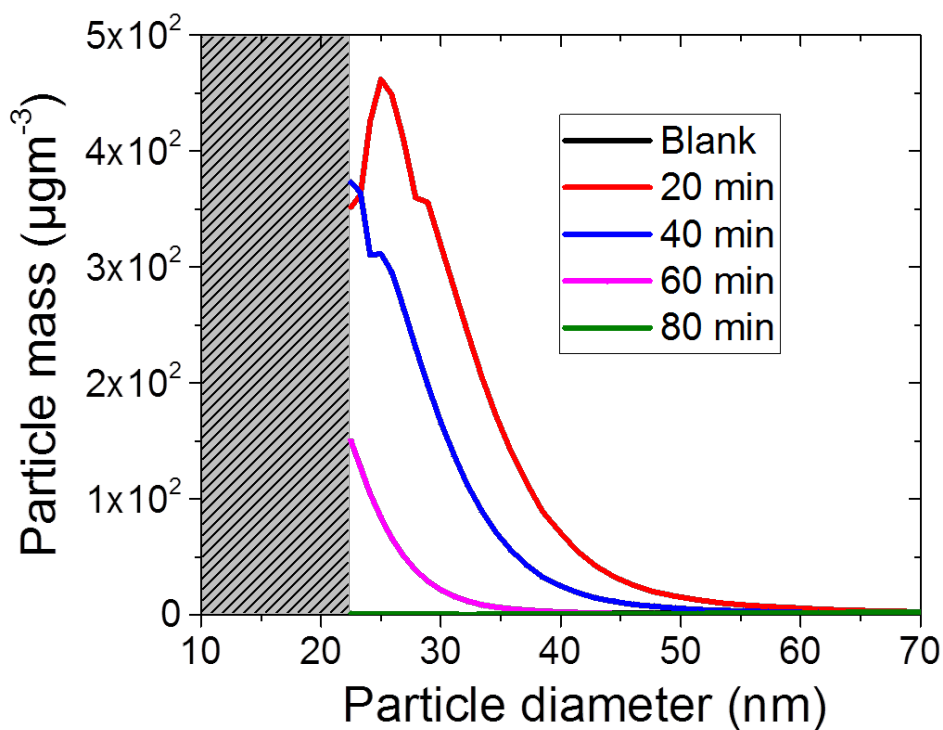
**Figure S2.** NO concentration raw data from films with lamps on (marked with yellow shading) and off at 35% RH and containing 4 mg of IC and 76.8 mg of CA with an iodide concentration of  $1.3 \times 10^{-5}$  M.



**Figure S3.** NO concentration raw data to show NO loss with lights on and HONO trap in line, and w/o the molybdenum converter, to allow differentiating between the NO loss resulting from the reaction with HO<sub>2</sub> and the secondary loss from the reaction with OH. The film used contained 4 mg of IC and 76.8 mg of CA equilibrated to 40% RH.

### 3. I<sub>2</sub>O<sub>5</sub> particles measurements

The measurement of the mass of I<sub>2</sub>O<sub>5</sub> was performed by using a Scanning Mobility Particle Analyzer (SMPS) based of a home-made Differential Mobility Analyzer (DMA) and a Condensation Particle Counter (CPC, Model 3775). The distribution is shown in Fig. S4 for different times. The SMPS as used was not allowing us to measure particles below 20nm of diameter.



**Figure S4.** Mass size distribution of I<sub>2</sub>O<sub>5</sub> particles produced from the oxidation of I<sub>2</sub> released at different times. The shady zone corresponds to the zone of the distribution we could not measure due to the limitations of the SMPS system.

#### 4. Modelling

All reactions considered in the model and the corresponding rate coefficients are listed in Table S1. The excitation rate (R1) was obtained by integration of the product of the spectrum of the UV lamps with the absorption spectrum of IC (Figure S1). We took an intersystem crossing efficiency of one for IC, which is the upper limit of intersystem crossing in triplet forming chromophores (Lamola and Hammond, 1965). The rate coefficient of the quenching of the triplet (R2) by O<sub>2</sub> was taken as an approximation from Canonica et al. (Cannonica, 2000). The measurement of R3 and the guess of R4 are explained in our previous work (Corral-Arroyo, 2018). Note that in that study the rate coefficients and adjustable parameters of the model were optimized to agree with the measurements in the humidity range of 35±2 % RH, overlapping with the RH range of the present study. The rate coefficients of the reaction between the triplet of IC and iodide and bromide (R5) were taken from Tinel et al. (Tinel, 2014) Maillard et al. (Maillard et al., 1983) determined the rate coefficients of reactions between organic radicals and oxygen, finding values within  $(1-5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Based on this study, we assumed a rate coefficient for the reaction between the ketyl radical and O<sub>2</sub> (R6) to be  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The rate coefficient of the reaction of HO<sub>2</sub> with itself (R7) was taken from Bielski et al. (Bielski et al., 1985). We took the rate coefficients of the reaction R8-11 given in Table 1 available in the literature from several references (Bianchini and Chiappe, 1992; Ishigure et al., 1988; Morrison et al., 1971; Nagarajan and Fessenden, 1985), and we kept them fixed. We considered the reaction between HO<sub>2</sub> and halides species (X<sup>•</sup>, X<sub>2</sub><sup>-</sup>, X<sub>2</sub>) with rate coefficients as given in the literature (Bielski et al., 1985; Ishigure et al., 1988; Schwarz and Bielski, 1986; Wagner and Strehlow, 1987) and we used them as a first guess. We took the rate coefficients available in the literature of the reactions involving halide radicals and HO<sub>2</sub> (R11-15) and we used them as a first guess but they were tuned down to get a better fit with the experimental

data. This tuning is reasonable since protic solvents increase the rate coefficients of reaction involving radicals or excited states, whereas organic solvents do not affect those reactions. There is evidence that hydrogen bonded transition states are involved in electron transfer (IvkovicJensen and Kostic, 1997), proton coupled electron transfer, hydrogen abstraction reactions (Mitroka et al., 2010) and quenching reactions between triplets and salts (Kunze et al., 1997). We assumed that the rate coefficient of the reaction between HO<sub>2</sub> and I<sup>•</sup> and the reaction between HO<sub>2</sub> and I<sub>2</sub><sup>-</sup> to give O<sub>2</sub> and iodide are equal to the one of the reaction between HO<sub>2</sub> and I<sub>2</sub><sup>-</sup> to give HO<sub>2</sub><sup>-</sup>. We considered the rate coefficient of the reaction between Br<sub>2</sub><sup>•-</sup> and Br<sup>•</sup> equals the one of the self-reaction of Br<sup>•</sup>. We assumed that X<sub>3</sub><sup>-</sup> has the same reactivity as X<sub>2</sub>. The photolysis rate of iodine was calculated by integrating the irradiance spectrum (Fig. S1) and the iodine photolysis spectrum (Choi et al., 2012) resulting in a rate of 0.01 s<sup>-1</sup>.

$D_{HO_2}$  was set to  $3.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ , Estimated using data of HO<sub>2</sub> production in absence of halides as a function of film thickness(Corral-Arroyo, 2018). This value is about an order of magnitude higher than that based on  $D_{H_2O}$  data of Lienhard et al. (200x). Assuming that  $D$  is inversely proportional to the radius of the diffusing molecule (Stokes-Einstein, eq. 1), we made a prediction of  $D_{Br_2}$  and  $D_{I_2}$ , leading to  $D_{Br_2} = 3 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  and  $D_{I_2} = 2 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ .

$$D = \frac{k_B T}{6\pi\eta r} \quad (\text{Eq. 1})$$

Equation 1 shows the Stokes-Einstein relation, where  $D$  is the diffusion coefficient,  $k_B$  is the Boltzmann constant,  $T$  is temperature,  $\eta$  is viscosity and  $r$  is the apparent radius of the molecule that diffuses.

As in our previous work (Corral-Arroyo, 2018), we represented the release due to diffusion by a simple first order loss rate coefficient ( $k_{diff}$ ) as:

$$k_{diff} = \frac{D}{\text{Film thickness}}$$

**Table S1.** Chemical reactions and the corresponding rate coefficients used for the model and the corresponding to their each reference.

Reaction number	Rate coefficient	Reaction	Rate coefficient (M <sup>-1</sup> s <sup>-1</sup> ) <sup>1</sup> ) (Br/I)	Rate coefficient (M <sup>-1</sup> s <sup>-1</sup> ) (Br/I)	Reference
R1	k <sub>IC</sub>	$\text{IC} \xrightarrow{h\nu} \text{IC}^{3*}$	1·10 <sup>-3</sup>	1·10 <sup>-3</sup>	Corral-Arroyo
R2	k <sub>scav-t</sub>	$\text{IC}^{3*} + \text{O}_2 \rightarrow \text{IC} + {}^1\text{O}_2$	3·10 <sup>9</sup>	2.6·10 <sup>9</sup>	Canonica
R3	k <sub>decay</sub>	$\text{IC}^{3*} \rightarrow \text{IC}$	6.5·10 <sup>5</sup>	6.5·10 <sup>5</sup>	Corral-Arroyo
R4	k <sub>CA</sub>	$\text{IC}^{3*} + \text{CA} \rightarrow \text{ICH} + \text{CA}^*$	90	90	Corral-Arroyo
R5	k <sub>hal</sub>	$\text{IC}^{3*} + \text{X}^- \rightarrow \text{ICH} + \text{X}^*$	6.27·10 <sup>6</sup> /5.33·10 <sup>9</sup>	6.27·10 <sup>6</sup> /5.33·10 <sup>9</sup>	Tinel
R6	k <sub>ICH</sub>	$\text{ICH} + \text{O}_2 \rightarrow \text{IC} + \text{HO}_2$	1·10 <sup>9</sup>	1.5·10 <sup>9</sup>	Maillard
R7	k <sub>HO2</sub>	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	8·10 <sup>5</sup>	8·10 <sup>5</sup>	Bielski
R8	k <sub>x1</sub>	$\text{X}^* + \text{X}^- \rightarrow \text{X}_2^{-*}$	9·10 <sup>9</sup> /1.1·10 <sup>10</sup>	9·10 <sup>9</sup> /1.1·10 <sup>10</sup>	Nagarajan/Ishigure
R9	k <sub>x2</sub>	$\text{X}_2^{-*} + \text{X}^* \rightarrow \text{X}_3^-/\text{X}_2$	8.4·10 <sup>9</sup> /8.4·10 <sup>9</sup>	-/8.4·10 <sup>9</sup>	Ishigure
R10	k <sub>x3</sub>	$\text{X}^* + \text{X}^* \rightarrow \text{X}_2$	3·10 <sup>9</sup> /1.9·10 <sup>10</sup>	-/1.9·10 <sup>10</sup>	Ishigure
R11	K <sub>eq</sub>	$\text{X}_2 + \text{X}^- \leftrightarrow \text{X}_3^-$	2.7·10 <sup>4</sup> E/768 <sup>E</sup>	2.7·10 <sup>4</sup> E/768 <sup>E</sup>	Bianchini/Morrison
R12	k <sub>scav1</sub>	$\text{HO}_2 + \text{X}^* \rightarrow \text{O}_2 + \text{HX}$	8·10 <sup>3</sup> /5·10 <sup>6</sup>	1.6·10 <sup>8</sup> /-	Wagner
R13	k <sub>scav2</sub>	$\text{HO}_2 + \text{X}_2^{-*} \rightarrow \text{O}_2 + 2 \text{X}^-$ + H <sup>+</sup>	8·10 <sup>3</sup> /5·10 <sup>6</sup>	1·10 <sup>8</sup> /-	Wagner
R14	k <sub>scav3</sub>	$\text{HO}_2 + \text{X}_2^{-*} \rightarrow \text{HO}_2^- + \text{X}_2$	8·10 <sup>3</sup> /5·10 <sup>6</sup>	9.1·10 <sup>7</sup> /4·10 <sup>9</sup>	Wagner/Ishigure
R15	k <sub>scav4</sub>	$\text{HO}_2 + \text{X}_2 \rightarrow \text{O}_2 + \text{X}_2^{-*} + \text{H}^+$	8·10 <sup>3</sup> /1·10 <sup>5</sup>	1.5·10 <sup>8</sup> /1.8·10 <sup>7</sup>	Bielski/Schwarz
R16	k <sub>scav5</sub>	$\text{X}_2 \xrightarrow{h\nu} 2 \text{X}^*$	-	<b>0.01</b>	<b>Calculated/Choi</b>

Source of rate coefficients: (Bianchini and Chiappe, 1992; Bielski et al., 1985; Canonica, 2000; Choi et al., 2012; Corral-Arroyo, 2018; Ishigure et al., 1988; Maillard et al., 1983; Morrison et al., 1971; Nagarajan and Fessenden, 1985; Schwarz and Bielski, 1986; Tinel, 2014; Wagner and Strehlow, 1987) \*First order rate coefficient. <sup>E</sup>Equilibrium constant

We set the differential equations shown below based on the mechanism (Table S1) and took the rate coefficients as described above. We calculated the concentration of the different chemical species and the production and release of HO<sub>2</sub> for several conditions assuming steady state.

$$\left(\frac{d[\text{IC}^{3*}]}{dt}\right) = k_{\text{IC}}[\text{IC}] - k_{\text{decay}}[\text{IC}^{3*}] - k_{\text{scav-t}}[\text{O}_2][\text{IC}^{3*}] - k_{\text{CA}}[\text{CA}][\text{IC}^{3*}] - k_{\text{hal}}[\text{X}^-][\text{IC}^{3*}] = 0$$



$$\left(\frac{d[ICH]}{dt}\right) = k_{CA}[CA][IC^{3*}] + k_{hal}[X^-][IC^{3*}] - k_{1ICH}[O_2][ICH] - k_{scav1}[X^-][ICH] = 0$$

$$[IC^{3*}] = \frac{k_{IC}[IC]}{k_{decay} + k_{scav-t}[O_2] + k_{CA}[CA] + k_X[X^-]}$$

$$[ICH] = \frac{k_{CA}[CA][IC^{3*}] + k_{syr}[X^-][IC^{3*}]}{k_1[O_2]}$$

$$\left(\frac{d[HO_2]}{dt}\right) = k_{ICH}[O_2][ICH] - k_{scav1}[X^*][HO_2] - k_{scav2}[X^-][HO_2] - k_{scav3}[X_2^-][HO_2] - k_{scav4}[X_2^-][HO_2] - 2k_{HO2}[HO_2]^2 - k_{diff}[HO_2] = 0$$

$$\left(\frac{d[X^*]}{dt}\right) = k_X[X^-][IC^{3*}] - k_{x1}[X^*][X^-] - k_{x2}[X_2^-][X^*] - k_{x3}[X^*]^2 - k_{scav1}[X^*][HO_2] = 0$$

$$\left(\frac{d[X_2^-]}{dt}\right) = k_{x1}[X^*][X^-] - k_{x2}[X_2^-][X^*] - k_{scav2}[X_2^-][HO_2] - k_{scav3}[X_2^-][HO_2] + k_{scav4}[X_2][HO_2] = 0$$

$$\left(\frac{d[X_2]}{dt}\right) = k_{x3}[X^*]^2 + k_{x2}[X_2^-][X^*] + k_{scav2}[X_2^-][HO_2] + k_{scav4}[X_2][HO_2] - k_{diff2}[X_2] - k_{scav5}[X_2] = 0$$

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