Supplemental Information

Heterogeneous photochemistry of imidazole-2-carboxaldehyde: HO₂ radical formation and aerosol growth

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NO₂ actinometry

The actinic flux (photons cm⁻² sec⁻¹) was measured with one, three, five and all seven lamps of the photo reactor turned on using NO₂ actinometry (method A), and independent measurements of the photon actinic flux (method B). With method A, NO₂ in a N₂/O₂ gas mixture was added to the flow-tube under two different configurations: a) a bare glass flow-tube, and b) a blank coated flow-tube consisting of CA only, in the absence of IC. The NO₂ gas was produced from the oxidation of a gas flow of NO through a chromate salt reservoir, shown in Fig. 1A. In configuration a), the concentration of NO₂ was about 8 ppbv and in configuration b) it was about 40 ppbv. NO₂ actinometry is based on the following reaction:

\[ NO₂ + hν \rightarrow NO + O\left(^3P\right) \]  (R1)

The photolysis constant, \( J \), in our case was treated as first-order rate constant, which quantifies the rate of photolysis of NO₂, \( J_{NO₂} \), in terms of a relative concentration change over time. The decrease in NO₂ was measured by the LED-CE-DOAS (Setup 1) and by the chemiluminescence (Setup 2); the NO₂ signal was allowed to stabilize, and lights were turned on sequentially. \( J_{NO₂} \) was calculated using the measurements and the following equation:

\[
J_{NO₂} = \frac{d \ln[NO₂]}{dt} = -ln\left(\frac{[NO₂]_t}{[NO₂]_0}\right) = J_{NO₂} \times t \]  (S1)

With all seven lamps turned on, the \( J_{NO₂} \) was about \( 2 \times 10^{-2} \) s⁻¹ (Setup 1) and \( 1 \times 10^{-2} \) s⁻¹ (Setup 2). This is about 2-3 times the ambient \( J \) at mid-latitudes under summer noon-time conditions. The \( J_{NO₂} \) for configurations a) and b) are compared in the Fig. S2, and agreed within 8% at 7 lamps and this variability increases as the number of lamps (irradiation) decrease, up to a factor of 2 as a maximum.
The $J$-values of NO$_2$ were calculated using independent measurements of the photon actinic flux of the UV lamps, which had been determined by B. Bohn at Forschungszentrum Jülich (Germany) with a LICOR 1800 hemispherical, cosine corrected spectro-radiometer (method B). The following equation was used to calculate the first order photolysis rate, $J$-value:

$$ J - value = \int_{300}^{420} F_{FT}(\lambda) \sigma(\lambda) \Phi(\lambda) d\lambda \quad (S2) $$

where $F_{FT}(\lambda)$ is the actinic flux measured in our flow-tube system, $\sigma(\lambda)$ is the NO$_2$ cross section at 294 K in cm$^2$ molecule$^{-1}$ (Vandaele et al., 2002), and $\Phi(\lambda)$ is the quantum yield data used from Sander et al., 2011. The $J$-values for NO$_2$ for methods A and B are compared in Fig. S2, and agree within a factor of 2 (higher $J_{NO2}$ for method A). The photon actinic flux shown in the Fig. S3 has been adjusted by this factor, and is compared with a typical solar spectral irradiance at the Earth surface (solar zenith of 48°, The American Society for Testing and Materials, ASTM).

**Equation S1** shows the relationship between the loss of NO$_2$, the derived pseudo-first order $J_{NO2}$ and the uptake coefficient ($\gamma$) for a heterogeneous reaction in a cylindrical flow-tube:

$$ \frac{d[NO_2]}{dt} = -JNO_2[NO_2] \quad JNO_2 = \frac{\gamma <c>[\frac{S}{\gamma}]}{4} \quad (S3) $$

where $<c>$ is the NO$_2$ mean molecular speed, $(8RT/\pi M)^{1/2}$, and $[\frac{S}{\gamma}]$ is the surface area of the film per gas volume ratio in our flow-tube system. These calculations are represented in Fig. S4.
**Figure Captions**

**Figure S1**: Determination of the NO concentration in the 2014 PSI flow-tube system. The lifetime of HO\textsubscript{2} is short enough at 500 ppbv with respect to its reaction with NO. This ensures a 1 NO:1 HO\textsubscript{2} molecular reaction in our experimental conditions. An IM/AC ratio of 0.088 was fixed for this specific experiment.

**Figure S2**: NO\textsubscript{2} j-values in s\textsuperscript{-1} from the bare glass and citric acid blank coated flow-tubes in Setup 1.

**Figure S3**: Solid line: the cross-section of IC in H\textsubscript{2}O; the UV-VIS absorption of IC was measured by Kampf et al., 2010 and interpolated to more recent molar extinction measurements by Barbara Nozière at IRCELyon (right scale in cm\textsuperscript{2}). Shaded gray: calculated wavelength dependent photolysis frequencies of imidazole-2-carboxaldehyde, j-values, based on the calculated quantum yield in our flow tube. Dotted line: actinic flux of the UV-light source in our flow-tube system from 300-420 nm range, the total flux is 2.26 \times 10^{16} photons cm\textsuperscript{-2} s\textsuperscript{-1}. Dashed line: a solar actinic flux spectrum for a solar zenith angle of 48°, 37° tilt towards the sun and clear skies (~2 \times 10^{16} photons cm\textsuperscript{-2} s\textsuperscript{-1} between 300-420 nm) obtained from the standard spectrum of the American Society for Testing and Materials (ASTM).

**Figure S4**: The photosensitized uptake coefficient of NO\textsubscript{2} (blue diamonds, right axis); this graph shows the inefficiency of NO\textsubscript{2} to compete with O\textsubscript{2} at atmospheric mixing ratios. The open red circles represent the CA blank measurements, the closed red circles represent a 1.725 [IC] \times [CA] film measurements during NO\textsubscript{2} actinometry experiments (left axis).
Figure S1
Figure S2
Figure S3
Figure S4