Supplement of

Light-induced protein nitration and degradation with HONO emission

H. Meusel et al.

Correspondence to: Y. Cheng (yafang.cheng@mpic.de) and H. Su (h.su@mpic.de)

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Kinetic study according to the Langmuir-Hinshelwood mechanism:

The Langmuir-Hinshelwood mechanism describes the kinetics of a heterogeneous (catalytic) reaction. The reactants, here NO$_2$ and H$_2$O, firstly adsorb reversibly to the catalytic surface, here protein (eq. S1). Usually water is sufficiently present in the atmosphere, and hence the protein surface would always be coated with water. Hence in this study the adsorption of water is not considered to be a significant rate limiting reaction step. Based on the experiments we conclude that there are two different ways of the transformation of adsorbed NO$_2$ to HONO. One is the direct light dependent conversion of NO$_2$ on the surface (eq. S2) and the other is the HONO formation during the light induced decomposition of nitrated proteins, which were produced in situ (eq. S3). In a last step the generated HONO is released from the surface (eq. S5).

Combining of the single reaction steps (equations S1, S2+S3= S4, S5) an effective reaction can be expressed (eq. S6).

Adsorption of NO$_2$ to the surface: \[ \frac{d[NO_2]_s}{dt} = k_1 * [NO_2]_g \] (eq.S1) where $k_1$ indicate the effective rate constant for the adsorption (adsorption – desorption), and index $s$ and $g$ indicate sorbed and gaseous state, respectively.

Heterogeneous NO$_2$ conversion on the surface: \[ \frac{d[HONO]_s}{dt} = k_2 * [NO_2]_s \] (eq.S2) where $k_2$ indicate the rate constant of the heterogeneous conversion of NO$_2$ to HONO

HONO formation via protein nitration and decomposition of nitrated proteins: \[ \frac{d[HONO]_s}{dt} = k_4 * k_5 * [NO_2]_s \] (eq.S3) where $k_4$ indicate the rate constant of the nitration of the protein and $k_5$ the rate constant of the degradation of the nitrated protein.

As these two processes cannot be discriminated by the observations presented here, we combine both reactions to formulate an overall formation equation (eq.4) with $k' = k_2 + k_4 * k_5$

\[ \frac{d[HONO]_s}{dt} = \frac{d[HONO]_s}{dt} + \frac{d[HONO]_s}{dt} = k' * [NO_2]_s \] (eq.S4)

Release of the generated HONO from the surface to the air (since proteins are in general slightly acidic, the desorption of HONO ($k_3$) should be fairly fast): \[ \frac{d[HONO]_g}{dt} = k_3 * [HONO]_s \] (eq.S5)

An effective formation rate of gaseous NO$_2$ to gaseous HONO $k_{eff}$ was calculated according to eq.6. \[ \frac{d[HONO]_g}{dt} = k_{eff} * [NO_2]_g \] (eq.S6) with $k_{eff} = k_1 * k' * k_3$