Supporting Information

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SI Text

Methods. *NO, NO₂, and HONO detection.* A THERMO 42C chemiluminescence analyzer was used for NO and NO_2 detection. The latter is based on the reaction between nitric oxide (NO) and ozone (O_3), which produces a characteristic luminescence with an intensity that is linearly proportional to the NO concentration. Nitrogen dioxide is transformed into NO by means of a molybdenum NO_2-to-NO converter in order to be measured with the chemiluminescent reaction. As HONO is detected by the instrument as NO_2, a denuder tube ($9 \ cm \times 0.95 \ cm$ i.d.) containing K_2CO_3/Na_2CO_3 (Fluka) was introduced between the exit of the flow reactor and the detector. The denuder can be either bypassed leading to the detection of NO and NO_2 together with HONO; or it can be switched into the sample line along the experiment. In that case, only NO and NO_2 can be measured after HONO removal from the gas stream. Therefore, the HONO concentration can be obtained as the difference of the detector signal without and with the carbonate denuder in the sampling line (1).

Periodical calibrations of the NO_2 from the bottle were performed using the carbonate denuder. Only 3% of the total NO_2 (and possible contaminants) was trapped in the denuder, this value was then considered in the calculation of the uptake coefficients and products yield.

Estimation of *NO₂ photodissociation.* NO_2 may photodissociate with unit quantum yield in the wavelength region emitted by the lamps (300–420 nm), but its loss in the gas phase is negligible for the residence time of 6 seconds used in our experiments. An estimation of the photolysis rate constant, $J = 6.52 \times 10^{-4} s^{-1}$ gives rise to a loss of 0.4% of the total NO_2 (g).

Uptake coefficient. The kinetic behaviour of the NO_2-soot heterogeneous reaction both in the dark and under irradiation can be well described by assuming a pseudo first-order reaction with respect to the gas-phase NO_2 concentration. The first-order rate constant, k_{obs}, derived from the experiment, is related to the geometric uptake coefficient (γ_g) by

$$\frac{d}{dt} \ln \frac{C_0}{C_i} = k_{obs} = \frac{\gamma_g <c_{NO_2}>}{2 r_{tube}} \qquad [1]$$

where r_{tube}, γ_g, t, and $<c_{NO_2}>$ are the flow-tube radius (0.547 cm), the geometric uptake coefficient, the exposure time, and the NO_2 average molecular velocity, respectively. C_0 is the NO_2 concentration when there is no contact between the soot surface and the reagent, whereas C_i is the trace gas concentration when the contact with NO_2 is allowed. The uptake coefficient is defined as the fraction of effective collisions between a gas phase reagent and a reactive surface that lead to the loss of the gas phase reagent due to chemical reaction. As γ_g is a mass dependent parameter (Fig. S2), it was transformed into a mass independent one, γ_{BET}, by taking into account the entire BET surface area of the soot sample instead of the geometric surface area of the glass substrate.

Equation I does not take into account possible diffusion limitations caused by the formation of a radial concentration gradient in the gas phase, which would occur if the loss at the surface is too fast to be recovered with the reagent supply. As a consequence, the Cooney–Kim–Davis method was used to correct the calculated uptake coefficients for gas-phase diffusion (2, 3). The diffusion coefficient, D, was calculated by using the formula proposed by Fuller et al. (4).

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2. Cooney DO, Kim SS, Davis EJ (1974) Analyses of mass-transfer in hemodialyzers for laminar blood-flow and homogeneous dialysate. *Chem Eng Sci* 29:1731–1738.
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4. Fuller EN, Ensley K, Giddings JC (1969) Diffusion of halogenated hydrocarbons in helium. The effect of structure on collision cross sections. *J Phys Chem* 73(11): 3679–3685.
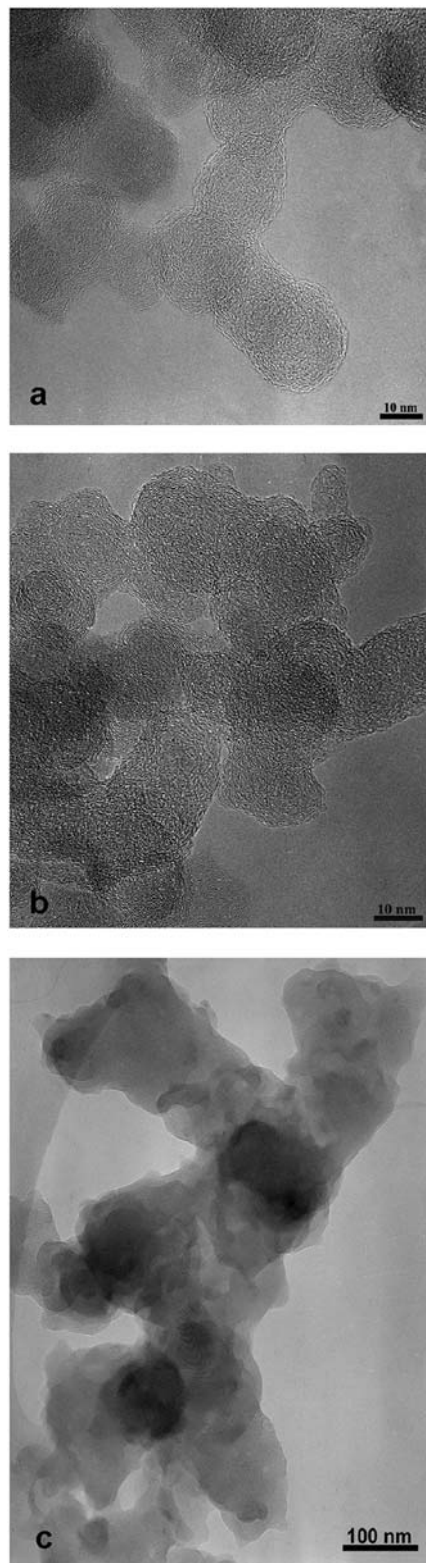
Fig. S1. TEM images of propane soot generated with a lean flame (a), a stoichiometric flame (b), and a rich flame (c).

Fig. S2. Mass dependence of the geometric uptake coefficient for the reaction of NO_2 with soot when soot particles produced under stoichiometric combustion conditions were exposed towards 25 ppbv of NO_2 under irradiation.

Fig. S3. Spectral features relevant to the study. The solid line shows the irradiance of the six lamps used in the experiments; the dotted line corresponds to the solar irradiance, and the dashed line and the right-hand axis displays the soot absorbance spectrum for particles produced with a rich flame.