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Laboratory studies of key gas-phase HO_x-NO_x coupling reactions.

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The HO_x (OH & HO_2) and NO_x (NO & NO_2) families of atmospheric radicals are coupled via a number of gas-phase reactions. These reactions have a substantial impact by controlling radical propagation / termination in catalytic cycles, so modifying the oxidation power of the atmosphere and its rate of O_3 production. However, field measurements {1-3} have demonstrated that our understanding of HO_x - NO_x chemistry is incomplete. We have identified four reactions (R1-R4) where the database is particularly unsatisfactory, leading to large uncertainties in atmospheric models {4-5}.

HO_2 + NO -> OH + NO_2 (R1a)
HO_2 + NO (+ M) -> HNO_3 (+ M) (R1b)

NO_2* + H_2O -> NO_2 + H_2O (R2a)
NO_2* + H_2O -> OH + HONO (R2b)

NO_3* + H_2O -> NO_3 + H_2O (R3a)
NO_3* + H_2O -> OH + HNO_3 (R3b)

OH + HNO_3 -> H_2O + NO_3 (R4)

In this experimental work, laser-based kinetic and spectroscopic tools were used to investigate recent observations {6-7} of HNO_3 formation from the (otherwise radical propagating) HO_2 + NO (R1), and OH formation following absorption of abundant, long wavelength photons by NO_2 {8} and NO_3 in the presence of water vapour (R2, R3). Uncertainties {9} associated with a classical HO_x–NO_x coupling reaction (R4) were also addressed. Critical photochemical parameters so derived have included absolute rate coefficients for (R1) and (R4) and product yields (R1b, R2b, R3b). The atmospheric implications of these results will be discussed.

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