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The photolysis of ortho-nitrophenols: A new gas phase source of HONO

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Formation of nitrous acid (HONO) in the gas phase has been observed for the first time in a flow tube photoreactor upon irradiation (300-500 nm) of 2-nitrophenol and methyl substituted derivatives using a selective and sensitive instrument (LOPAP) for the detection of HONO. Formation of HONO by heterogeneous NO2 photochemistry has been excluded, since production of NO2 under the experimental conditions is negligible. Variation of the surface to volume ratio and the nitrophenol concentration showed that the photolysis occurred in the gas phase indicating that HONO formation is initiated by intramolecular hydrogen transfer from the phenolic OH group to the nitro group. From the measured linear dependence of the HONO formation rate on the reactant's concentration and photolysis light intensity, a non-negligible new HONO source is proposed for the urban atmosphere during the day. Unexpectedly high HONO mixing ratios have been observed recently in several field campaigns during the day. It is proposed that the photolysis of aromatic compounds containing the ortho-nitrophenol entity could help to explain, at least in part, this high contribution of HONO to the oxidation capacity of the urban atmosphere.