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The photolysis of alkyl nitroaromatics: A new gas phase source of HONO

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Nitroaromatics are of particular interest since they possess carcinogenic and phytotoxic properties and have been implied to play a role in forest decline. In a recent study in our laboratories formation of nitrous acid (HONO) from the photolysis of nitrophenols has been shown for the first time. HONO is of major significance in tropospheric chemistry since the photolysis leads to the formation of OH radicals. Recent field studies have demonstrated that the contribution of HONO to the oxidation capacity of the atmosphere has been underestimated and point to the existence of yet unknown daytime sources of HONO.

Formation of nitrous acid (HONO) in the gas phase was studied in a flow tube photoreactor upon irradiation (300-500 nm) of ortho-nitrotoluenes and derivatives, using a selective and very sensitive instrument (LOPAP) for the detection of HONO. Photochemical formation of HONO was observed upon irradiation for the first time, which was linear correlated to the gas phase concentration of the nitrotoluenes. Variation of the surface to volume ratio and the nitrotoluenes concentration showed that the photolysis occurred in the gas phase. The huge difference on the HONO formation between 2- and 3-nitrotoluene supports that HONO formation is initiated by intramolecular hydrogen transfer from the ortho-alkylic CH_3 group to the nitro group. Contribution of photolysis of aromatic compounds containing the ortho-nitrotoluene to the oxidation capacity of the urban atmosphere will be discussed.