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Validation of an experimental setup to study atmospheric heterogeneous ozonolysis of semi-volatile organic compounds

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Abstract. There is currently a need for reliable experimental procedures to follow the heterogeneous processing simulating the atmospheric conditions. This work offers an alternative experimental device to study the behaviour of semi-volatile organic compounds (SVOC) that presumably exhibit extremely slow reactivity (e.g. pesticides) towards the atmospheric oxidants such as ozone and OH. Naphthalene was chosen as a test compound since it was widely studied in the past and hence represents a good reference. Prior to ozone exposure, the gaseous naphthalene was adsorbed via gas-solid equilibrium on silica and XAD-4 particles. Then, the heterogeneous reaction of ozone with adsorbed naphthalene was investigated in specially designed flow tube reactors. After the reaction, the remaining naphthalene (adsorbed on particles surface) was extracted, filtered and analyzed by Gas Chromatography-Flame Ionization Detector (GC-FID). Thus, the kinetics results were obtained following the consumption of naphthalene. Using this procedure, the rate constants of heterogeneous ozonolysis of naphthalene ($k_{O_3, \text{silica}} = 2.26 (\pm 0.09) \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and $k_{O_3, \text{XAD-4}} = 4.29 (\pm 1.06) \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) were determined for silica and XAD-4 particles, at 25°C and relative humidity <0.7%. The results show that the nature of the particles significantly affects the kinetics and that heterogeneous ozonolysis of naphthalene is faster than its homogeneous ozonolysis in the gas phase.

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