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A comparison of radical and non-radical conversion rates of SVOCs in the tropospheric condensed phase

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Secondary formation pathways of organic compounds are currently intensely discussed including conversions in tropospheric aqueous particles as well as cloud droplets. Particularly, SVOCs (Semivolatile Organic Compounds) and their reaction products are expected to be potential precursors for the formation of higher molecular organic compounds. In the aqueous phase, such compounds can undergo both various oxidative processes (radical and non-radical oxidants reactions) and non oxidative processes (aldol, acetal, dimerisation and ester formation reactions). These chemical aqueous phase processes are expected to be very efficient proceeding on short timescales and produce multifunctional organic compounds of less volatility. However, the importance of non-radical reactions compared to currently known radical oxidations under different conditions has not yet been assessed .Current aqueous phase mechanisms such as CAPRAM (Chemical Aqueous Phase RAdical Mechanism; Herrmann et al., 2005) do consider radical oxidation processes of organic compounds.

In the present study, a comparison of radical and non-radical conversion rates of organics in cloud droplet and aqueous particles is performed for both urban and remote environmental conditions. For the comparison, available reaction rate constants have been used together with outcome of recent model simulations (Tilgner and Herrmann, 2010) using the CAPRAM 3.0i mechanism. First order-conversion rate constants in the aqueous phase for cloud and aqueous particle conditions, for (i) OH, (ii) NO_3, (iii) H_2O_2, (iv) the aldol condensation, (v) the dimerisation and (vi) the ammonium-catalysed accretion reactions were calculated with the available, at current quite restricted data set. From the comparison, it is concluded that organic accretion reactions might be of interest in some cases but generally do by far not reach the oxidative conversion rates of radical and non-radical oxidants. Particularly, the adol condensation reactions can sometimes be partly competitive with radical oxidation reactions and might, to some extend, act as a non-oxidative pathway for less volatile organics with aldehyde functionalities. Additionally, reactions of H_2O_2 with easily oxidisable SVOCs such as glyoxal and pyruvic acid are shown to be competitive to the OH radical conversions when H_2O_2 is not being strongly depleted by sulphur(IV).

References:

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