



The potential role of organic peroxides in laboratory new particle formation

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New particle formation in the atmosphere belongs to the currently most discussed aspects of atmospheric aerosols with significant implications for cloud formation and microphysics, once these particles have grown beyond about 50 nm in particle diameter. If these particles act as cloud condensation or ice nuclei they can affect the radiation budget at the Earth's surface and cause climate couplings important to understand when aiming to predict climate change scenarios. One aspect widely discussed is the potential contribution of organic trace gases from anthropogenic and biogenic sources. From earlier studies it is known that secondary ozonides formed in the reaction of carbonyl compounds and the so-called stabilised Criegee Intermediates (stabCI) act as nucleation inducing molecules. However their gas-phase concentration prevents their activation. Because of that additional compounds are required for activation and subsequent growth at the very smallest sizes with a strong Kelvin effect present. Here we focussed on the role of organic peroxy radicals (RO_2) and the so-called stabilized Criegee Intermediate (stabCI) in laboratory new particle formation during ethene-ozone reactions in the presence of excess nopinone. Ethene was used because of its well-known chemical reactions. In order to check the influence of RO_2 , the peroxy radicals were varied by the addition of different nitrogen oxide concentrations. A flow-chamber set-up in a walk in cold chamber was used at atmospheric pressure and room temperature. 176 ppb of ethene and 543 ppb of nopinone were dispersed in a synthetic air flow of 20 L min^{-1} . Additionally varying mixing ratios of ozone (87-108 ppb) and of nitrogen oxide (0.5-100 ppb) have been added, too. The total particle number concentration ($D_p > 2.7 \text{ nm}$) was monitored at a fixed reaction time of 147 s at the end of the tube. The observed particle number concentrations could be reproduced by gas phase and aerosol nucleation kinetics with an organic nucleation mechanism reasonably well. This mechanism assumes the nucleation to be started by secondary ozonides (SOZ) and activated by either organic peroxy radicals or the stabCI with a preference to the RO_2 molecules from nopinone-OH oxidation. This indicates that high molecular weight radicals are likely to play a significant role in organic new particle formation at least in the laboratory. In general we observed a clear reduction of particles activated when increasing NO up to a nearly suppression at an NO mixing ratio of 100 ppb. This reduction appeared in three distinct sections: (a) a first one at low NO mixing ratios ($\text{NO} < 20 \text{ ppb}$), in which the nucleation cores (SOZ) have been activated mainly by RO_2 , (b) a second one at larger NO mixing ratios ($20 \text{ ppb} < \text{NO} < 90 \text{ ppb}$), where the SOZ was activated predominantly by the stabilized Criegee Intermediates and (c) the final one, in which nucleation was nearly suppressed. The results imply that organic peroxy radicals which are ubiquitous in the atmosphere could be important agents in activating nucleation inducing (reactive) molecules. However there are other important aspects worth to mention: (I) The activation seems possible only for larger RO_2 radicals but not for instance for the smallest ones. (II) the role of atmospheric NO_x is complex: High NO reduces RO_2 , but high NO_2 might lead to elevated ozone production during daytime and thus to and elevated production.