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Validation of a new flow-reactor for the study of secondary organic aerosol (SOA) formation

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Aromatic and biogenic compounds known to be relatively abundant in the atmosphere are usually easily oxidized by common tropospheric species (OH, O₃, NO₃), which contributes significantly to the formation of low vapor pressure products, considered as the main precursors of SOA. In order to improve the understanding of SOA formation mechanisms, a new flow reactor has been developed in our laboratory to study the early stages of particle formation.

The controlled flows of ozone and volatile organic compound enable stable concentrations in the reactor and provide a steady state of the reaction in the reactor and the conditions for pseudo-first order kinetics. By changing either the flow or the distance between the injector head and the sampling point, the concentrations at different reaction times can be measured, thus allowing deducing mechanistic and kinetic parameters.

The exhaust lines are used for collecting gaseous (on adsorbent cartridges subsequently analyzed by TD-GC/FID/MS) and particulate samples (number and size distribution of particles formed using a SMPS, average composition of the particles with an AMS). Using these various instrumental techniques combined with gas chromatographic analyses will permit the determination of the kinetics and the influence of various physical parameters on the chemical mechanisms of SOA formation.

The ozonolysis of a series of unsaturated alkenes (methylated pentenes) was chosen for kinetic validation, while the α -pinene, already well documented in the literature was chosen to validate the system and the analytical chain for both kinetic and particulate phase measurements. Results are presented and compared with those of the literature.

1. Experimental setup

The cylindrical reactor developed in the laboratory has been designed to work with total flows of about 1 to 3 L min⁻¹, corresponding to reactions times between 10 s and several minutes. A mobile injector is used to introduce the reagents separately and ensure their rapid mixing into the Pyrex tube with a 1-m length and a 10-cm i.d. section, in a laminar flow regime at atmospheric pressure and room temperature.

The injection head has been designed to allow good mixing of the reactive gases at transit times of seconds and to support the formation of a laminar flow into the reactor. To this end, the volume of the gas mixing chamber of the injection head was minimized by filling it with glass beads (diameter 2 mm).

The laminar flow in the reactor ensures a stationary mode. The volume of the flow reactor may vary depending on the position of the sliding injection head, in order to watch the evolution of the reagents and products at various reaction times, and to estimate kinetic and mechanistic parameters. Considering a fixed distance between the movable injection head and the sampling point, different reaction times may be achieved by changing the flow rate of the reactants in the reactor.

A canister containing tens of ppm of volatile organic compound (VOC) is used for the generation of a continuous gas flow with the help of a mass flow controller (MFC). The zero air is used as a carrier gas towards the injection head and also ensures the dilution of VOC at the requested level of concentration (Figure 1). A controlled flow of carbon monoxide is also added into the mixture of gasses as a scavenger of the OH radicals potentially formed in the ozonolysis processes. An ozone generator provides a controlled flow of oxidant (7.4×10^{12} to 4.4×10^{13} molecule cm^{-3} , ensuring pseudo-first order kinetic conditions) which reaches the injection head on a separate line.

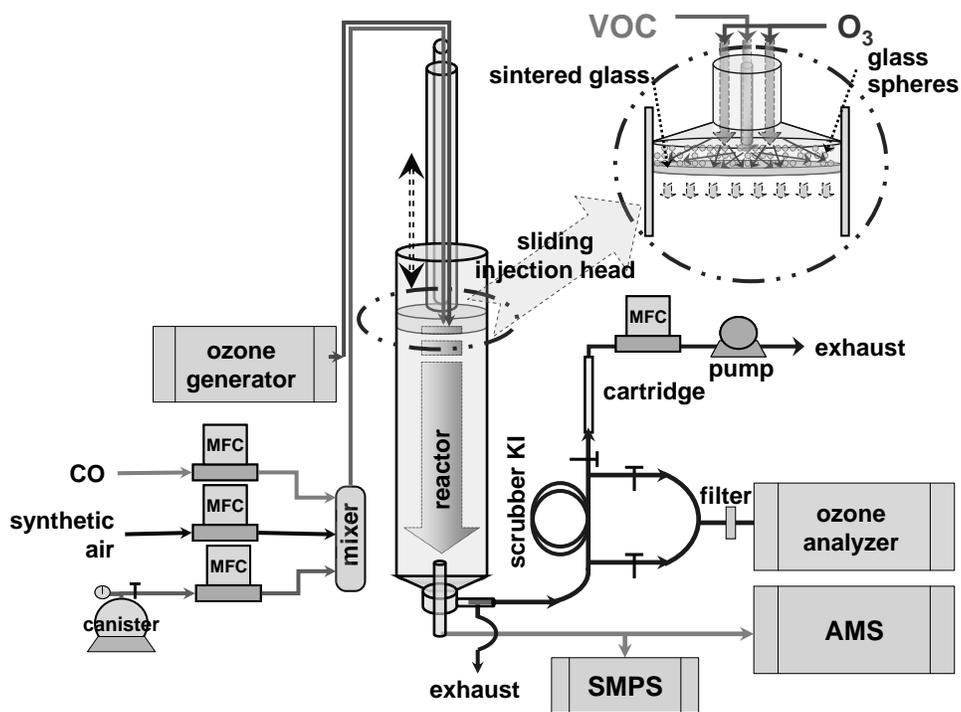


Figure 1. Schematic of the experimental setup

The outlet analytical chain of the reactor includes an AMS (Aerosol Mass Spectrometer), on the same sampling line with a SMPS (Scanning Mobility Particle Sizer) to analyze the particulate phase, and cartridges filled with three different adsorbents for the subsequent analysis of the gas phase. The AMS measures in real time the average chemical composition of aerosols as a function of their size. The SMPS is used to obtain complementary information concerning the size distribution of particles by coupling a differential mobility analyzer (DMA) and a condensation particle counter (CPC). The sampling strategy for the gas phase involves the exposure of a single cartridge at a time and the procedure is repeated in identical experimental conditions at least three times in order to estimate the concentration of compounds, but also the reproducibility and accuracy of sampling.

Ozone traps (scrubbers) consisting of a dry coating of KI on the walls of a copper tube are used upstream of the cartridge sampling in order to prevent additional degradation processes of the VOCs by ozone during sampling and thermal desorption. An O₃ analyzer monitors O₃ levels in the reactor as well as the efficiency of the scrubber.

Sampled cartridges are thermodesorbed and analyzed by gas chromatography coupled with mass spectrometry. Thermodesorption techniques were preferred over techniques requiring sample pretreatment. To optimize the analytical method in terms of detection sensitivity and result reproducibility, the glass insert of the chromatograph, where the thermodesorbed compounds are trapped prior to injection into the column, was tested in two different configurations: empty, in cryogenic conditions (-100 °C) and filled with a few mg of Carbopack B at a temperature of 0°C. By comparing the results of the ozonolysis of alpha-pinene (3.1×10^{12} molecule cm⁻³) in both configurations, there is an increase of detection sensitivity, reproducibility and linearity in the case of the filled insert. Moreover, the rate coefficient obtained for the ozonolysis reaction, $k = 1.1 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹, is closer to the recommended value than in the case of the cryogenic configuration, $k = 1.7 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ with the empty insert.

2. Kinetic study of VOC ozonolysis

Considering VOC ozonolysis in pseudo first order reaction conditions, where $[O_3] \gg [VOC]$, the integrated rate law can be written as:

$$\ln\left(\frac{[VOC]_0}{[VOC]_t}\right) = k't \quad (1)$$

According to this relation, the graph of the logarithm of the ratio between the initial concentration in VOC, $[VOC]_0$, and at time t $[VOC]_t$, as a function of the reaction time t , gives a slope $k' = k [O_3]$ (Figure 2). The obtained slope gives the value of the rate coefficient knowing the concentration of ozone in the reactor.

2.1 Ozonolysis of methylated pentenes

In order to validate the analytical chain and the kinetic measurements performed in the reactor, the ozonolysis of a series of unsaturated alkenes (methylated pentenes) was chosen. The ozonolysis reactions of 2,4,4-trimethyl-1-pentene (tM1P) and 2,4,4-trimethyl-2-pentene (tM2P) have been studied in excess of O₃.

The experimental results give the value of the rate coefficients considering an average concentration of ozone in the reactor of 1.8×10^{13} molecule cm^{-3} as obtained from a large number of measurements using a calibrated ozone analyzer.

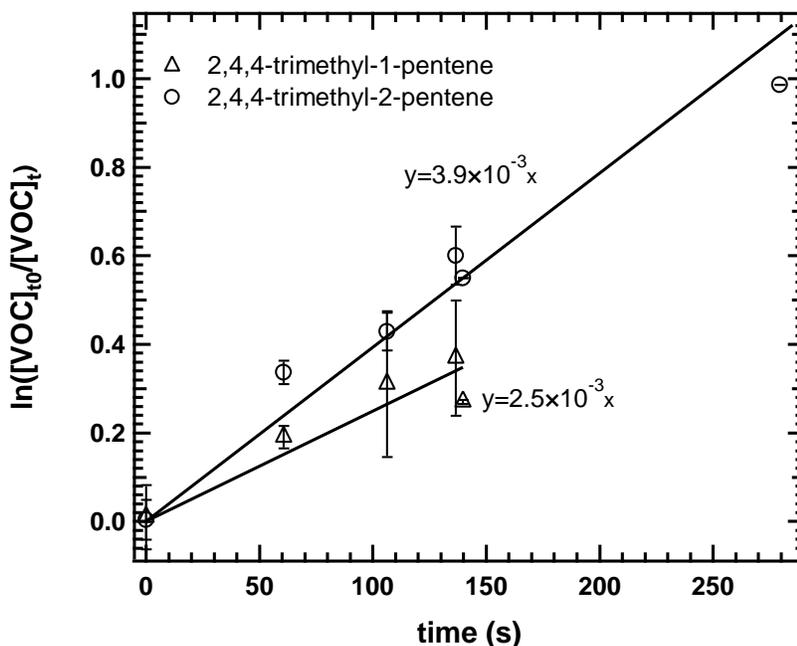


Figure 2. Kinetics of tM1P and tM2P ozonolysis - $[tM1P]_0 = 7.6 \times 10^{11}$ molecule cm^{-3} , $[tM2P]_0 = 7.6 \times 10^{11}$ molecule cm^{-3}

Given the experimental conditions a value of $k = 1.35 \times 10^{-16}$ cm^3 molecule $^{-1}$ s $^{-1}$ was calculated for the reaction of tM1P with ozone, while the similar reaction of tM2P present a higher reactivity with a determined value of $k = 2.11 \times 10^{-16}$ cm^3 molecule $^{-1}$ s $^{-1}$ (Figure 2). These results need to be completed with the same kinetic approach at different initial concentrations in reagents. These preliminary results are in good agreement with the literature in the case of tM2P ($k = 1.39 \times 10^{-16}$ cm^3 molecule $^{-1}$ s $^{-1}$, Grosjean, 1996), while for tM1P a significant difference can be observed, compared with the literature ($k = 9.73 \times 10^{-18}$ cm^3 molecule $^{-1}$ s $^{-1}$, Leather, 2010).

2.2 Ozonolysis of alpha-pinene

The ozonolysis of alpha-pinene is an important source of oxidized species, which contribute significantly to the atmospheric formation of SOA and its reaction rate coefficient has been estimated by many previous studies. The ozonolysis of alpha-pinene was carried out in the reactor at ambient temperature in dry air (RH ~ 0%).

With the same experimental setup and for $[O_3] = 3.4 \times 10^{13}$ molecule cm^{-3} , a value of $k = 1.1 \times 10^{-16}$ cm^3 molecule $^{-1}$ s $^{-1}$ for the rate coefficient of the reaction, in good agreement with

those in the literature (e.g. $k = 9.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Tillmann 2009) was determined (Figure 3).

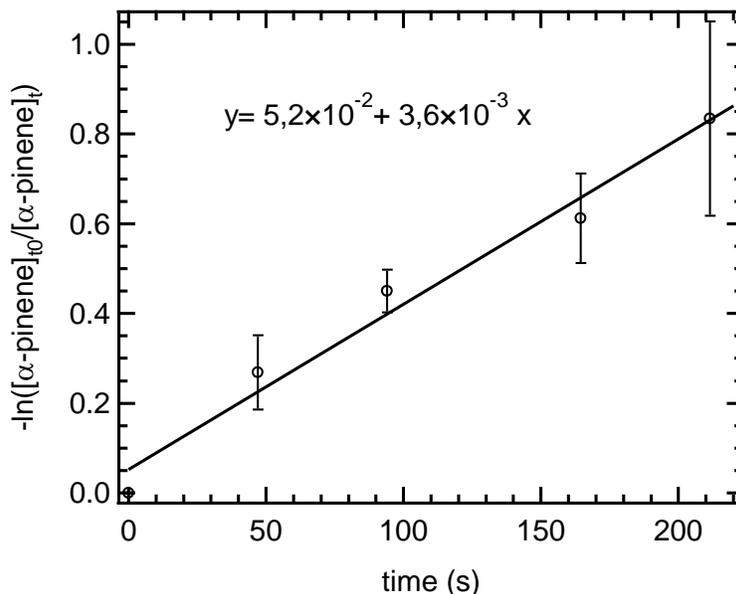


Figure 3. Kinetics of ozonolysis of alpha-pinene - $[VOC]_0 = 3.1 \times 10^{12} \text{ molecule cm}^{-3}$

3. Number / size standard distribution of aerosols

The distribution of aerosols generated in the ozonolysis of alpha-pinene was monitored as a function of reaction time using the SMPS.

The aerosol sampling was conducted using the central sampling tube of the flow reactor. The observed distribution of the particles formed after the nucleation processes is unimodal, fairly broad, and centered around 90 nm. It seems little influenced by the different reaction times ranging from 1.5 to 6 minutes. This suggests that during this period there is only one mode of particle formation and the processes of nucleation / coagulation are dominant. Further experiments are needed to confirm these results. It is planned to study the influence of some physicochemical parameters such as humidity on the particle formation, or the influence of preexisting aerosols into the reactor.

Finally, analyses using the AMS will allow to study the chemical composition of the formed aerosols. Connected to the same sampling line as the SMPS, it will provide complementary information on particle characterization (size distribution and chemical composition).

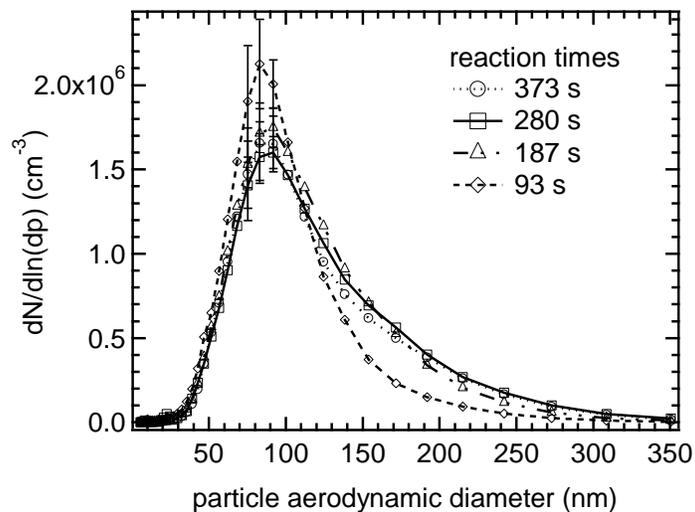


Figure 4. $dN/d\ln(dp)$ (cm^{-3}) as a function of particle diameter for different reaction times in the ozonolysis of alpha-pinene

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