



## **Atmospheric transformation of semivolatile industrial chemicals on aerosol particles in a cold environment: Smog chamber investigation of octadecylvinylether (ODVE) and its major transformation product on $\text{Al}_2\text{O}_3$**

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An aerosol smog chamber facility has been set up in a cold laboratory (4x5x6m) at temperatures down to  $-28^\circ\text{C}$ . The facility consists of a solar simulator (16 Osram Ever-sun Super fluorescent lamps, 80W each) and a cylindrical chamber (1 m diameter and 4 m height) with a volume of 3250 l, made of Duran glass. The chamber is irradiated from the bottom, and a small, negative temperature gradient is maintained in vertical direction for sufficiently fast mixing. The semivolatile compounds are exposed in the chamber as thin coatings on inert aerosol particles ( $\text{Al}_2\text{O}_3$  Alumina C, Degussa) to the typical active ingredients of tropospheric air: Simulated sunlight, humidity, ozone, OH radicals and all other components of a simulated atmosphere. The coatings are at sub-monolayer thickness in order to meet the condition of infinite dilution, required for an environmental relevance of an experimental simulation study. The large specific surface of the material ( $150\text{ m}^2/\text{g}$ ) caused by the small size (about 10 nm diameter) of the primary particles enables us to reach sub-monolayer thickness of the coating with portions of about 10-50% of the organic compounds; typical surface coverages of our experiments are 10% or less.

The UV absorption spectrum of octadecylvinylether (ODVE) was determined from solutions of 0.8% ODVE in n-hexane, methanol and acetonitrile and from the plain compound (ODVE techn., Aldrich, >85%), containing hexadecylvinylether (HDVE) as the main impurity (found to be 10%). The spectrum showed no solvent effect and

an exponential decrease of the absorption cross sections between 280 and 370 nm, falling from  $10^{-20}$  to  $10^{-22}$  cm<sup>2</sup>. The overlap with the solar spectrum and the solar simulator is extremely small, and direct photolysis can thus be neglected.

Coatings of ODVE were prepared by mixing with dichloromethane (that contained ODVE at a mass fraction of 1 % relative to the aerosol materials) and evacuating in a rotary evaporator at 40 Torr and room temperature. The dry materials were then dispersed in water that was atomized by a nozzle, employing a flow of hot air to fill the smog chamber (held at  $-15^{\circ}\text{C}$ ) with the aerosol, reaching final mass densities of 1 mg/m<sup>3</sup>. The aerosol was then sampled at regular intervals (50-100 L each) on Teflon filters. The filter samples were analyzed by gas chromatography (GC) for the ODVE content, by placing them into sample vials with 1 ml of n-hexane, ultrasonifying for 5 min, sedimenting for 5 min by a centrifuge and injecting 10  $\mu\text{l}$  into the GC each (Sichromat 2, Siemens; on-column injector and retention gap,  $l=2.5$  m, 0.32 mm I.D., SGE; quartz capillary column CP Sil 19 (Chrompack),  $l=13.5$  m, 0.22 mm I.D., 0.19  $\mu\text{m}$  film thickness, flame ionization detector). ODVE eluted at a retention time, RT (min), of 8.9. A recovery of ODVE around 40% was obtained from the coated powder, and a conversion product (possibly induced by hydrolysis) was observed at RT= 9.1. A similar product from HDVE (RT=8.05) was observed at RT=8.25.

Various smog chamber runs were performed at  $-15^{\circ}\text{C}$  at levels of OH up to  $3.3 \times 10^7$  cm<sup>-3</sup>, and blank runs were performed in the absence of OH and in darkness. The dark experiments delivered a loss rate constant for ODVE of  $2 \times 10^{-5}$  s<sup>-1</sup> and a larger value for HDVE. Even at the lowest level of  $[\text{OH}]=1 \times 10^6$  cm<sup>-3</sup>, ODVE disappeared rapidly ( $30 \times 10^{-5}$  s<sup>-1</sup>), and the signal dropped soon below the detection limit, due to either volatilisation or photochemistry on the particles. On the other hand, the rate constant for the reaction of the transformation (hydrolysis/autoxidation) product from the dark reaction of ODVE with OH radicals could be determined from the filter samples of the aerosol. A linear dependence of the decay rate of the ODVE product (corrected for the decay of the aerosol mass density) on OH exposure was observed, leading to a rate constant of  $k_{\text{OH}}=0.5 \times 10^{-11}$  cm<sup>3</sup>s<sup>-1</sup> at  $-15^{\circ}\text{C}$ .