

Capabilities and Limitations of Smog Chamber Techniques for Atmospheric Degradation Studies of Semivolatiles

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Introduction

The tropospheric transformation of gaseous organic compounds by photochemistry involving OH radicals and other reactive species is a well-known process. The existing data base is large for organic molecules¹ but rather limited for compounds with low vapour pressure, due to their strong tendency of adsorption to the walls of the kinetic equipment. Much less is known about such transformations of semi-volatile and aerosol-borne compounds^{2,3}. Catalytic and photocatalytic properties of the particles can enhance the transformation, although mineral aerosols and fly ash appear to be much less photoactive than synthetic, semiconducting materials, such as ZnO⁴, TiO₂ and Fe₂O₃^{5,6}. It appears that the presence of chloride-containing aerosol should be avoided in glass chambers since chloride can be activated to become highly reactive atomic chlorine, derived not only from the aerosol surface but also from the glass surface of the smog chamber after acid-enhanced volatilisation of HCl from the particles and deposition on the glass walls⁷. Chlorine-containing compounds are expected to release acid chlorides, which are hydrolysed in the presence of humidity on chamber walls, thus contributing to the HCl burden. Employing a set of gaseous compounds (alkanes and aromatics) with a wide range of rate-constant ratios, k_{OH}/k_{Cl} , is required in systems with chlorine-containing semivolatiles for detecting the presence of atomic Cl, that can then be distinguished from the reaction with OH⁸ and be suppressed by a large excess of alkanes.

The aerosol smog chamber technique takes advantage from the sticky properties of semivolatile compounds to be adsorbed on model surfaces. In order to avoid adsorption on the chamber walls, the compounds are adsorbed at sub-monolayer thickness on highly disperse, inert materials and are exposed to the constituents of a simulated atmosphere in the aerosol-borne state at room temperature. This technique has been pioneered in our laboratories at the Fraunhofer-Institute at Hannover from 1984, inspired by W. Stöber⁹, and the following reactions of OH radicals with semivolatile compounds have been studied at room temperature in a cylindrical glass vessel (1 m diameter, 3 m height), irradiated by a solar simulator consisting of 7 medium pressure lamps (Osram HMI, 1200 W each): di-(2-ethylhexyl)- phthalate (DEHP) on SiO₂¹⁰, Al₂O₃, Fe₂O₃ and fly ash from a coal power plant¹¹ and terbuthylazine (TBA)¹², pyrifenoxy¹³ and lindane (g-HCH) on SiO₂⁸. Because of a change of research directions at Hannover we were requested to de-install the aerosol chamber completely in 1999. On the other hand, a new research project was funded by the Federal Ministry of Environment in the year 2000 to develop simplified test methods for the atmospheric degradation of semivolatile compounds in relation to the POP convention¹⁴, where we initially followed the lines of an exposure of filter samples of coated aerosol particles to a simulated atmosphere in smaller glass vessels of a few 100 L, where we had determined relative rate constants of simazine, isoproturon and benzoic acid, using TBA as a reference¹⁵. It turned out that the access of OH radicals to the compounds was hindered by the dense packing of the aerosol particles (about 5-10 layers of particles on the filter) and that the migration of semivolatile compounds from deeper layers to the surface might have perturbed the kinetic observations and that volatilisation of lindane could not be controlled, even after cooling the vessel by 10°C¹⁶.

Construction of the aerosol smog chambers

Preparatory experiments were performed in a provisional 1750 L-chamber at our previous site, the Fraunhofer-Institute of Toxicology and Aerosol Research at Hannover (now Fraunhofer-Institute of Toxicology and Experimental Medicine). Two sections of the previous chamber were used to construct a smog chamber with 2 m height as an interim version. The provisional chamber was again irradiated from the top by a solar simulator, consisting of 14 fluorescent lamps Osram Eversun L80W/79R. Since it was not possible to maintain the negative temperature

EMV - Hemispheric and Global Distribution Dynamics of Persistent Organic Pollutants

gradient required for thermal gas circulation, mixing was enforced by a miniature fan (a standard CPU cooler from a PC). Cooling was achieved by enclosing the chamber into a 2.3 x 1.5 x 2.4 m box, constructed with a frame of wooden bars (6 cm thick) and thermally insulated from the laboratory by inner and outer layers of polyethylene film on the bar frame and an additional filling of the 6 cm space with Styrofoam (4 cm) at the side walls and closed by UV transparent Teflon film on the top (FEP 200A), from where the solar simulator irradiated the chamber. The box was cooled by a strongly ventilated heat exchanger, supplied with water/diethylene glycol cooling at 0 °C from an air cooled engine (Julabo 144, 9.8 kW) in the cellar of the building. A temperature of 6.5 °C was reached within 5 hours cooling time and was kept stable within $\pm 0.5^\circ\text{C}$ for the duration of the experiment.

At the new site of Bayreuth University the construction of a temperature-controlled, cold laboratory room (4x5x6 m) enables us to reach a temperature of -28°C and to construct an aerosol chamber with 3250 l volume (a vertical glass cylinder with 1 m inner diameter and a height of 4 m). By adding a new section to the existing ones, this final glass cylinder consists of four sections, sealed together with gaskets made of Teflon film (FEP 200A) and employs the same Teflon film as a window for the irradiation by the solar simulator. The solar simulator consists of 14 fluorescent tubes (Osram Eversun Super, 80 W each) and irradiates the chamber from the bottom. The heat of the solar simulator causes a vertical temperature gradient of about -1°C that improves mixing by the thermal circulation in the chamber. Since the principle of fluorescent lamps is based on low-pressure mercury lamps, the operation at low temperature causes problems by the decreased vapour pressure. Ignition of the lamps failed at temperatures below 0 °C. Starting the lamps at higher temperatures did not help since the discharge became faint at -10°C and extinguished below -15°C . It was thus decided to insulate the solar simulator by sheets of Teflon film and to control the temperature by regulating the air flow that cools the lamps.

Results and Discussion

Fig. 1 shows the residence times observed in the new chamber for the number densities of carrier particles (Aerosil 380, Degussa) as a function of their diameter. It can be seen that the maximum residence time exceeds one day at diameters between 500 and 800 nm.

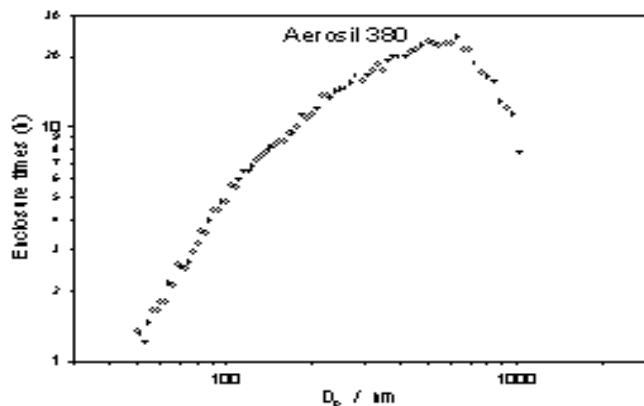


Fig. 1: Average residence times of SiO_2 particles as a function of diameter in a glass chamber with 1 m diameter and 4 m height.

It appears that larger particles are lost by sedimentation and that smaller particles are lost by diffusion to the walls of the vessel and by coagulation. This is similar to the behaviour of particles in the atmosphere, where a maximum residence time of 1 week is reached in the boundary layer of the lower troposphere, not exceeding one month in the middle troposphere at similar particle diameters according to Jaenicke, 1978³. The shorter residence times of particles in the chamber can be more than balanced in OH-exposure experiments by employing larger levels of OH, enhancing OH by more than two orders of magnitude, reaching 10^8 cm^{-3} for the duration of exposure.

DEHP, TBA, DDT, lindane and α -HCH were exposed¹⁷, adsorbed at sub-monolayer thickness on SiO_2 (Aerosil 380) to OH radicals in the 2 m-chamber at 6.5 °C. Further experiments on dicofol and hexabromo diphenylether (BDE 153)¹⁸ were performed. The consumption of the aerosol-borne compounds was determined by gas

chromatographic analysis from filter samples of the aerosol and was found to be exponential with time, where the decay rate was observed to be proportional to the level of OH, this defining a second order rate constant. In some experiments the level of OH, obtained from photochemical degradation of methyl nitrite, changed drastically during the exposure. In such cases the time integral of OH, characterising the exposure, dominated the observed consumption rate, leading to consistent results. On the other hand, the loss of lindane and α -HCH from the aerosol contributed almost 50% to the observed consumption at OH-levels of 10^7 cm^{-3} , perturbing the kinetic analysis. The predominating evaporation at room temperature might be a reason why our previous measurement for lindane⁸ is in disagreement with the present one. On the other hand, a measurement at elevated temperature (75-150°C) in the gas-phase¹⁹ extrapolates to much lower values for the two HCHs. Fig. 2 shows the rate constants observed for DEHP and TBA in an Arrhenius diagram (right hand scale), including an additional value obtained for TBA by the new chamber at 2 °C. One can recognise immediately that the activation energy for TBA is much smaller than the enthalpy of evaporation. DEHP even has a slightly negative activation energy. This behaviour indicates that indeed the aerosol-borne compounds react with OH and that any contribution of the vapour is unimportant.

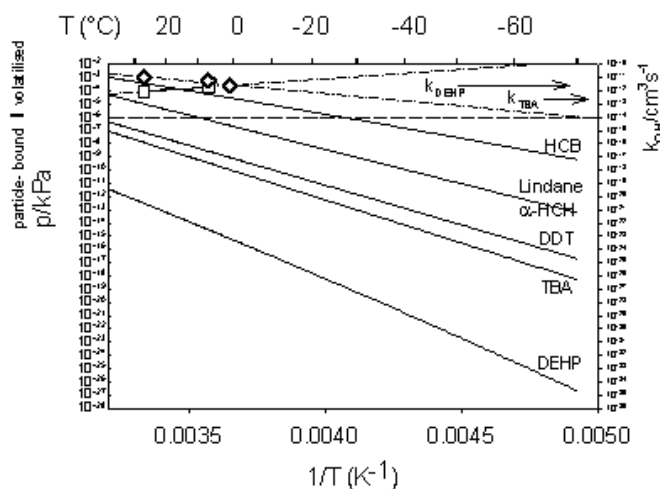


Fig. 2: Vapour pressures of typical, semivolatile compounds (left hand scale) and rate constants observed for DEHP and TBA (right hand scale, dash-dotted lines). The horizontal, dashed line marks the border between gaseous and aerosol-borne compounds. It appears that the new chamber might enable us to study hexachlorobenzene (HCB) at -28°C .

On the other hand, the porosity of environmental aerosols might impede the access of OH to the semivolatiles, and shielding effects by water and co-adsorbed compounds may retard the transformation²⁰. This shielding effect has attracted the interest in models of atmospheric long-range transport of such compounds, where the partitioning between gas and particle phase²¹ is thought to have a decisive effect by neglecting the transformation in the particle-borne state²². It appears that other techniques, such as coated-wall flowreactors^{23, 24}, may add information in this unexplored field.

Such studies are needed for the polycyclic aromatic hydrocarbons and other toxic air contaminants; they are still desirable for several of the persistent organic pollutants (POPs) of the Stockholm convention and they may be required for a testing of chemicals within the EU directive REACH. The so-called "dirty dozen" has now been banned, but are we on the safe side with other existing and new chemicals?

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