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Aerosol fast flow reactor for laboratory studies of new particle formation

Michael J. Ezell, Haihan Chen, Kristine D. Arquero, Barbara J. Finlayson-Pitts *

Department of Chemistry, University of California Irvine, Irvine, CA 92697-2025, USA

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ABSTRACT

Understanding the fundamental mechanisms of new particle formation and growth (NPFG) is critical to the development of accurate quantitative models of atmospheric particulate matter. Challenges to elucidating the chemistry of these processes include accessing a variety of well-controlled experimental conditions approaching the point of new particle formation, and having an inexpensive system which can be reproducibly maintained with low levels of contaminants from previous runs and other sources. We describe here the design and characterization of a flow tube reactor for such studies, and its initial application to NPFG from the reaction of the gas phase precursors methanesulfonic acid and trimethylamine in the absence or presence of added water vapor. Insights into some of the fundamental processes involved in NPFG that could not be obtained in earlier studies using our large volume, slow flow system are described.

1. Introduction

Airborne particles are of great interest due to their impacts on visibility (Hinds, 1999), human health (Heal et al., 2012; Mauderly & Chow, 2008; Pope III & Dockery, 2006) and climate (Finlayson-Pitts & Pitts, 2000; Hinds, 1999; IPCC, 2013; Pandis & Seinfeld, 2006). While there are direct emissions of particles, a large component is formed from reactions of precursor gases to form low volatility products (Donahue et al., 2009; Hallquist et al., 2009; Holzinger et al., 2007; Pöschl, 2005; Zhang et al., 2012) that either form new particles or add to existing ones to grow them to sizes of ~100 nm where they scatter light and act as cloud condensation and ice nuclei. The nature of these precursors and the reactions are not well established. It is known that SO_2 formed from the combustion of fossil fuels as well as the oxidation products of organosulfur compounds are converted in air to H_2SO_4 which, in the presence of water, ammonia and/or amines, forms particles (Chen et al., 2012; Kuang et al., 2008; McMurry, 1980; Riipinen et al., 2007; Zhang et al., 2012; Zollner et al., 2012). However, the fundamental kinetics and mechanisms involved have not been fully elucidated. Furthermore, there are other potential precursors such as methanesulfonic acid (MSA, CH_3SO_3H) (Dawson et al., 2012) formed simultaneously with H_2SO_4 in the organosulfur oxidations, as well as higher molecular mass organic products formed from the oxidation of volatile organic compounds (VOC) in air (Ehn et al., 2014; Lee & Kamens, 2005; Zhao et al., 2013). Finally, it is not known if there are synergistic interactions of organics with sulfuric acid/or MSA, to enhance or inhibit new particle formation and growth (Dommen et al., 2013; Kulmala et al., 2013; Zhang et al., 2012). A full understanding of such issues on a molecular basis is central to the development of accurate models of particle formation and their growth in air.

* Corresponding author. Tel.: +949 824 7670; fax: +949 824 2420.
E-mail address: bjfinlay@uci.edu (B.J. Finlayson-Pitts).

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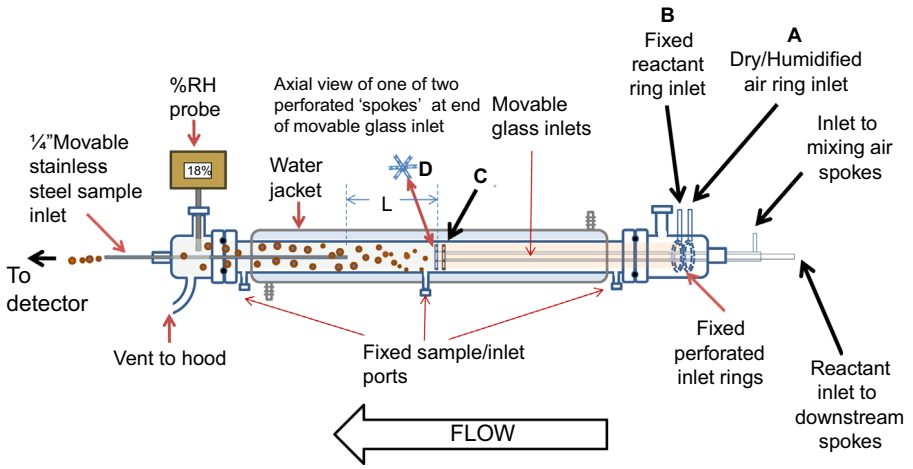

Fig. 1. Fast flow reactor schematic.

Probing new particle formation and growth in well-controlled laboratory systems is challenging. As such, a variety of experimental approaches is needed to cover particle formation and growth from the earliest stages (with reactions times of seconds) up to growth to hundreds of nanometers with much longer reaction times from several minutes to hours. For the latter, we have previously described a large volume, slow flow system (Ezell et al., 2010) with residence times from 4 to 120 min. Here we describe a fast flow system with variable residence times in the flow tube from 0.2 to 30 s.

Ideally, one would like to study these reactions at sufficiently short reaction times to follow the earliest stages of particle formation under conditions free of contaminants. The latter is especially difficult, particularly with some chamber surfaces such as Teflon that take up and release species, often reversibly (Matsunaga & Ziemann, 2010; Zhang et al., 2014). This may not be a significant problem if the concentrations of species released from the chamber walls are small relative to the reactant concentrations, but it limits how far the precursor concentrations can be lowered without potentially risking such interferences. One approach to minimizing these problems is the use of reaction chambers made of non-porous, relatively unreactive materials such as glass that can be easily cleaned on a regular basis, and that also allow access to relatively short reaction times.

We describe here the design and characterization of a flow system that meets these criteria. In addition, we present some initial results on the formation of particles from the reaction of MSA with trimethylamine (TMA, $(CH_3)_3N$) that demonstrate the utility of this approach.

2. Aerosol flow system design

The aerosol fast-flow system (Fig. 1) designed to cover relatively short reaction times from 0.2 to 30 s (not including sampling time; see below) was fabricated from borosilicate glass. The major section has an inside diameter of 7.6 cm and a total length of 1.3 m with a water-jacketed section 1.1 m long. At either end of this main section are two end-caps mated to the central tube with clamps and sealed by O-rings.

The upstream end cap is 10.5 cm in length and holds two perforated hollow glass rings that serve as fixed inlets for reactants and dry or humidified air. These 6.7 cm o.d. rings are both formed from one centimeter o.d. glass tubing and are perforated by thirty-six, evenly spaced 0.05 cm holes to disperse air and reactant gases (see Fig. 1, inlets A and B). The upstream cap also secures and guides two concentric glass tubes that serve as movable inlets for either reactants and/or dry or humidified air, with an overall length of 78 cm. Each of these concentric tubes terminates in six 0.5 cm diameter glass 'spokes' that efficiently disperse reactant and mixing air in the radial direction through four 0.05 cm holes in each of the six spokes. The set of spokes that is furthest downstream relative to the overall flow (inlet D, Fig. 1), serves as the inlet for one of the reactant gases and has small holes directed upstream towards the other set of spokes (inlet C, Fig. 1), 1.0 cm away, which carries mixing air. The perforations in inlet C are directed so as to transect the overall flow and serve to provide a turbulent regime for efficient mixing of reactant gases coming from the inlet D as well as species from the upstream fixed rings.

The smaller end cap at the downstream end of the flow tube is 6.5 cm in length and guides a stainless-steel $\frac{1}{4}$ in. sampling tube that is 76 cm in length and is aligned along the major axis of the flow tube. This end cap also has a $\frac{1}{2}$ in. tube to vent the majority of the gas and particle flow. Both end caps also have a sealable $\frac{1}{2}$ in. port to hold a relative humidity/temperature probe. These large removable caps facilitate cleaning of the flow tube in about an hour. Finally, the main body of the flow tube also has three $\frac{1}{4}$ in. glass ports for additional sampling or inlets, one at each end and a third located midway along the length of the water-jacketed portion of the flow tube. The flow tube total volume is 5.9 L and total surface area is 3.11×10^3 cm^2, resulting in a surface to volume ratio of 0.53 cm^{-1}.