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Chapter 4

Preparation of Experiments: Addition and In Situ Production of Trace Gases and Oxidants in the Gas Phase



David M. Bell, Manuela Cirtog, Jean-François Doussin, Hendrik Fuchs, Jan Illmann, Amalia Muñoz, Iulia Patroescu-Klotz, Bénédicte Picquet-Varrault, Mila Ródenas, and Harald Saathoff

Abstract Preparation of the air mixture used in chamber experiments requires typically the injection of trace gases into a bath gas. In this chapter, recommendations and standard protocols are given to achieve quantitative injections of gaseous, liquid or solid species. Various methods to produce ozone, nitrate radicals and hydroxyl radicals are discussed. Short-lived oxidants need to be produced during the experiment inside the chamber from pre-cursor species. Because highly reactive oxidants like hydroxyl radicals are challenging to detect an alternative method for the quantification of radical concentrations using trace molecules is described.

4.1 Introduction

In order to obtain useful data from simulation chamber experiments, reliable and reproducible additions of reactants such as volatile organic compounds (VOCs) and inorganic compounds are required. The most suitable method depends on the physical

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properties of the compound and on the specific chamber geometry and operational mode. The injection method should ensure homogeneous mixing, avoid contamination or memory effects of the reaction mixtures and avoid interferences of secondary processes. In addition, the goal of the specific experiment and properties of instruments used for the analysis (sensitivity and sampling frequency of instruments) need to be considered. Thus, the injection procedure needs to be carefully chosen and should be well characterized.

Typically, the injection of stable compounds is achieved by transporting small amounts of reagents into the chamber together with a high gas flow of nitrogen or synthetic air using a specialized inlet system. Although gaseous and liquid reagents can be often directly injected into the chamber (Fig. 4.1), homogeneous mixing can be challenging, if reagents are introduced at one point in the chamber. Most chambers are therefore equipped with fans to ensure rapid mixing. Because oxidants such as OH and NO₃ radicals are short-lived and highly reactive so that they cannot be stored, they need to be produced during the experiment from stable precursor compounds.

In this chapter, the addition of gaseous, liquid, and solid organic and inorganic compounds into a chamber and methods for the in situ production of oxidants are described.

4.2 Injection of Gaseous Compounds

Small amounts of pure gases (<10 cm³) can be directly injected with a gas-tight syringe straight through a septum in the inlet system of the chamber (Fig. 4.1). The gas is then flushed into the chamber together with a high flow of the bath gas. Alternatively, the injection port with the septum can be directly mounted on the chamber wall. In order to ensure rapid mixing, it is useful to have the injection port located close to a fan (Fig. 4.1). For an accurate estimation of the injected volume, the dead volume of the needle of the gas syringe needs to be determined, because the gas in the needle is also injected into the chamber. The dead volume can be measured by weighing the syringes when only the needle is filled with pure water whose density was determined in advance (for the appropriate laboratory temperature).

The resulting mixing ratio (c_{reactant}) of the injected compound inside the chamber can be calculated using the ratio of the injected volume (V_{reactant}) and the volume of the reaction chamber (V_{chamber}):

$$c_{\text{reactant}} = \frac{V_{\text{reactant}}}{V_{\text{chamber}}} \quad (4.2.1)$$

The accurate preparation of mixtures at the ppbv level can be difficult if a small sample volume is required. The manual injection with gas-tight syringes is not always precise and can limit the reproducibility of experiments. As an alternative, six-way valve systems (not shown on Fig. 4.1) replacing the syringe injection port allow more accurate and precise injections of reagent volumes as low as a few tenths of microliters.

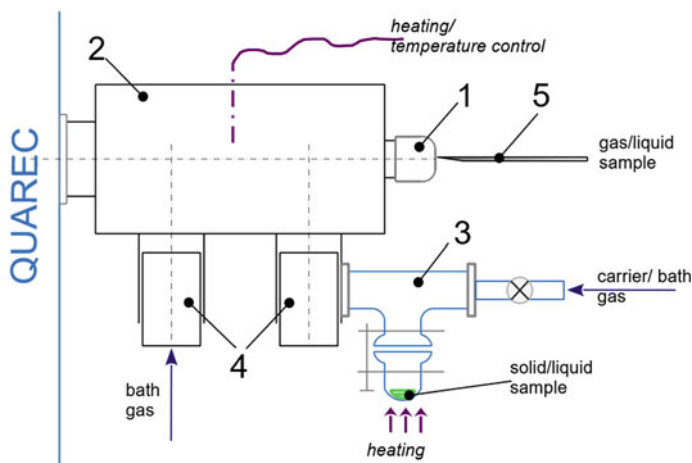


Fig. 4.1 Means of additions of stable molecules into the atmospheric chamber QUAREC (University Wuppertal): (1) injection port for syringes, (2) heated injection block, (3) alternative device for the addition of low volatile liquid or solid samples, (4) valves for bath gases and (5) syringe. Schematics by Iulia Patroescu-Klotz, BUW

High concentrations of reactive gases in the chamber, for example, needed to scavenge OH radicals in ozonolysis experiments, can be achieved by directly flowing pure gases or gas mixtures from gas cylinders equipped with pressure regulating valves into the chamber via an inlet system. The gas flow into the chamber can be controlled by flow metres or flow controllers and pressure gauges. The volume of the injected reagent can be calculated using the measured flow rate (F) and the injection time (t):

$$V_{\text{reactant}} = F \times t \quad (4.2.2)$$

In this case, the accuracy of the injected volume is limited by the accuracy of the measured flow rate and the injection time. If flow controllers based on thermal measurement of the flow rate are used, the thermal capacity of the specific gas may need to be considered to derive the actual flow rate.

Alternatively, the reagent gas samples can be prepared (purified and/or dried) in a vacuum line. The reagent gas can then be prepared in a glass bulb. The total concentration can be calculated from its volume (V_{bulb}) and the pressure in the bulb (p_{bulb}) and the chamber (p_{chamber}) measured with an appropriate manometre:

$$C_{\text{reactant}} = \frac{V_{\text{bulb}} \times p_{\text{bulb}}}{V_{\text{chamber}} \times p_{\text{chamber}}} \quad (4.2.3)$$

The bulb can be connected to the inlet system and the material is flushed into the chamber. The bulb should be thoroughly cleaned before use, either by pumping or by cleaning it with a solvent and then drying it in an oven for several hours.

Vacuum lines can include a series of bulbs to prepare small quantities of the reagent by successive dilution into a gas bath followed by a pressure reduction. In this case, the concentration is obtained by calculating the dilution from the ratio of the pressure values in the glass bulbs. Therefore, the use of very precise and reliable pressure gauges becomes critical for the accurate calculation of the resulting concentration. The advantage of applying successive dilution steps is that the pressure in the bulbs remains in a range that can be accurately measured by standard pressure gauges.

Determination of the resulting concentration of the injected compound in the chamber can be done *in situ*, e.g., by spectrometric methods, online (gas-chromatography or similar methods) or offline. It is also worth checking for blank values before the initial injection and checking for memory effects, particularly for 'sticky' substances. The use of short and heated Teflon tubes in the inlet system is recommended for the injection of these compounds. Preparing diluted mixtures can also help to achieve a quantitative injection. Injections via flow controllers should be avoided for these compounds because they are prone to memory effects and may become clogged or damaged.

4.3 Injection of Compounds from Liquid Sources

Reagents that are liquid at room temperature can be injected into the simulation chamber with similar systems like gaseous reagents. The optimum method depends on the vapour pressure and stability of the compound. It is worth noting that the partial pressure of the compound inside the chamber needs to be lower than the saturation vapour pressure of the reagent at the chamber temperature.

The simplest method is using a syringe, with which the compound is injected into a bath gas stream in a heated inlet system, where the liquid rapidly evaporates and is transported into the chamber. This is particularly applicable for moderate to low vapour pressure compounds. Caution is recommended for sticky compounds. The resulting concentration in the reaction chambers is

$$c_{\text{reactant}} = \frac{V_{\text{inj.}} \times \rho \times P \times N_A}{M \times V_{\text{chamber}}} \quad (4.3.1)$$

with $V_{\text{inj.}}$ = injected volume of the liquid compound; ρ = density of the liquid compound; P = purity of the compound sample; N_A = Avogadro's number; M = molar mass of the compound; V_{chamber} = volume of the chamber.

The precision and reproducibility of injections using syringes with volumes in the low micro-litre range are low. Part of the liquid can be lost due to evaporation from the glass syringe between preparation and injection and the dead volume of

the needle affects the injected volume similar to the injection of gaseous compounds (Sect. 4.2). For calibration purposes, pure compounds can be dissolved in a suitable solvent, in order to obtain high-diluted solutions that ensure that the desired amount of organic compound is transferred without losses into the gas phase inside the chamber (Etzkorn et al. 1999). This can increase the accuracy, with which the injected volume is known, and minimize losses. Caution has to be taken that the solvent does not affect the experimental results nor the measurement of trace gases. There are also commercial solutions available for the evaporation of compounds solved in liquids into an air flow. An example is the Liquid Calibration Unit (LCU) provided by the company IONICON that was designed for the calibration of mass spectrometer instruments. Flows are accurately controlled by mass flow controllers to produce well-defined concentrations of the reactants in the air that is provided. However, using flow controllers is only feasible for some solvents and works best for water. This limits the application of the LCU to certain compounds.

The injection of liquid samples can also be achieved using permeation sources. Permeation tubes are commercially available or can be custom-built. A constant permeation rate is achieved if the tube is kept at a constant temperature. The compound is flushed at a well-defined rate from the permeation source into the chamber (Tumbiolo et al. 2005). The resulting concentration of the compound in the chamber can be accurately calculated from measured flow rates and the permeation rate that is determined from reference permeation sources or the measured weight loss of the compound in the permeation source.

One other method to introduce low-volatility compounds into the chamber is using a glass vial that is connected to the inlet system through a glass/stainless steel line (Fig. 4.2). The vapour above the liquid is flushed with the bath gas into the chamber. Evaporation can be enhanced by heating the vial. Lines are recommended to be cleaned before use, for example, by evacuating them or flushing them with clean dry air.

Similar to gaseous compounds, a vacuum line can be used to generate gaseous reagent samples in a glass bulb containing a well-defined concentration. The liquid reagent sample is placed in a glass vial that is attached to the line (Fig. 4.2). In order to remove volatile impurities from the sample, the reactant can be frozen with liquid nitrogen and the air is pumped away from the sample. The valve between the finger and the vacuum line is then closed and the Dewar flask is removed to evaporate impurities from the frozen sample. The sample is then again frozen with liquid nitrogen and the gaseous impurities are pumped away. Several cycles of this procedure may be required to achieve a high purity of the sample.

After the cleaning procedure, the reagent sample is thawed and the vapour above the liquid can be transferred into a glass bulb attached to the preparation line. The concentration can be determined from the pressure in the glass bulb as described for the preparation of gaseous mixtures (Eq. 4.2.3). Once the desired pressure is achieved both the finger and the bulb are disconnected from the prep-line and any residual reagent sample is then pumped away. The reagent in the bulb can be flushed into the chamber.

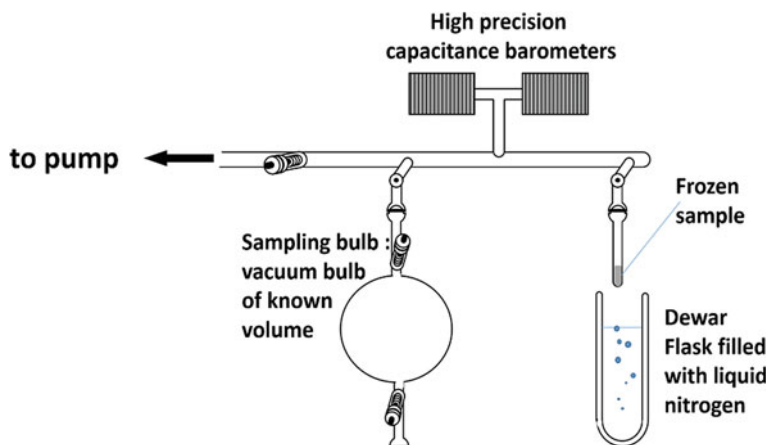


Fig. 4.2 Schematic representation of the vacuum line system used to remove impurities from liquid compounds and to prepare a glass bulb containing a well-defined concentration of the reactant

The effective concentration of low volatile compounds in the gas phase in the chamber can be lowered due to deposition on the surface of the inlet system and on the chamber wall near the inlet or due to condensation on particles. Re-evaporation can affect experiments at later times. The concentration can also be lower than expected if thermally unstable compounds decompose in the heated inlet or compounds form dimers if high concentrations are injected (for example, formic acid or acetic acid). These effects can be avoided or minimized by applying an appropriate temperature of the inlet system, by warming up the entire line system and by adjusting the flow with which the evaporated compound is transported into the chamber. Using a well-controlled heating system is recommended rather than using a heat gun. For example, the port for the injection of compounds in the QUAREC chamber at the University Wuppertal is housed in a metal casing which can be heated up to a temperature of 60 °C.

Water vapour is an essential part of the gaseous compounds in the atmosphere and its presence can affect various gas-phase reactions and specifically particles. Although it is a liquid at room temperature and therefore can be injected with similar methods as described above, the amount of water that needs to be introduced to reach atmospheric concentrations is much higher than that of other trace gases. Therefore, small impurities in the water used for the humidification can be an important source of contaminations in the experiment. Special precautions need to be taken not only regarding the generation of the pure water using, for example, a Milli-Q-water or Nanopure water device but also in the selection of all materials in the humidification system as well as of cleaning procedures and intervals. Particle formation can be an issue in the humidification system. They can be removed by heated stainless steel filters in the inlet system. In addition, atmospheric relative humidity is typically within the range of 20–80% so that a substantial fraction of air in the chamber needs to be exchanged to yield atmospheric water concentrations without condensation in

the humidification system, even if the system is heated to moderate temperatures. Therefore, the humidity of air cannot easily be changed during an experiment without diluting all trace gases.

Methods to humidify the air are:

- Boiling pure water and transporting the steam with a high gas flow into the chamber.
- Using a commercial humidification system such as the Control–Evaporation–Mixing (CEM) system by the company Bronkhorst. This system sprays a controlled flow of pure liquid water into a heated volume, in which the evaporated water is mixed with a controlled flow of dry air.
- Evaporating pure water into an evacuated chamber and flushing the water vapour into the chamber as described above. The system can be either made of glass or stainless steel and is recommended to be heated.
- Using a temperature-controlled Nafion tube. In this system, water molecules are transported through a membrane, if pure liquid water is on one side of the membrane and a dry gas flow is on the other side of the membrane.

4.4 Injection of Compounds from Solid Sources

Solid compounds can be introduced by flushing the vapour phase above the solid sample into the chamber similar to the method applied for liquids (Fig. 4.1). Controlling the temperature allows to adjust the concentration of the fraction of the compound in the gas phase. Heating can be achieved with a heat gun but needs to be carefully applied. Care must be taken to avoid that small parts of the solid material are flushed into the chamber due to thermal turbulence in the vial specifically if the vial is heated.

The resulting concentration of the reactant in the chamber can be calculated from the weight loss of the solid sample in the vial:

$$c_{\text{reactant}} = \frac{m \times P \times N_A}{M \times V_{\text{chamber}}} \quad (4.4.1)$$

with m = weight loss of the compound in the vial; P = purity of the compound sample; N_A = Avogadro's number; M = molar mass of the compound; V_{chamber} = volume of the chamber.

Removing impurities and preparation of glass bulbs containing a well-defined concentration of the compound can be similarly done as described for liquids except that there is no need for freezing (Fig. 4.2).

The transfer of the reactant from solid sources is often not quantitative due to condensation and deposition on the walls of the inlet system so that the resulting concentration in the chamber is lower than calculated from the weight loss. Similar to the injection from liquid sources, this can be minimized by heating the inlet system,

but specifically, compounds that are solid at room temperature may also be thermally unstable at higher temperatures.

In some very specific cases, the thermal decomposition of a solid polymer can be used to produce gaseous monomers. In these cases, the solid polymer is placed in the heated vial and the gaseous monomer above the solid sample can be flushed into the chamber. An example is the decomposition of solid paraformaldehyde $(\text{CH}_2\text{O})_n$ to formaldehyde (HCHO).

The injection of dissolved solids in aerosol particles is described in Chap. 5.

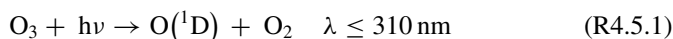
4.5 Production of Hydroxyl Radicals (OH)

The hydroxyl radical (OH) radical is the main oxidant of trace gases in the atmosphere (Stone et al. 2012). In the troposphere, the primary source of OH is mainly the photolysis of ozone, formaldehyde (HCHO) and nitrous acid (HONO) and the ozonolysis of alkenes. The study of OH oxidation processes in simulation chambers can provide kinetic data (e.g. reaction rate coefficients, Sect. 7.3), product yields of individual reactions or can be used to test entire reaction schemes. Due to the very short lifetime and high reactivity of OH, radicals cannot be stored but must be generated during the experiment. Sources for OH radicals in chamber experiments are often photolytic reactions like those occurring in the atmosphere. Precursor compounds such as ozone are introduced in the gas mixture. OH radical production from precursors can be accompanied by the formation of other reactive species such as NO, for example, in the case of the photolysis of HONO that can affect the chemistry in the experiment.

It is crucial for the design of OH oxidation experiments to consider the type of precursor used for the primary radical production and the effect of radical termination and radical regeneration reactions, which are closely connected to the presence of nitrogen oxides (NO and NO_2) in the air mixture (Sect. 4.5.7).

4.5.1 OH Production from Ozone Photolysis

Ozone photolysis in the presence of water vapour is the main source of OH radicals in the atmosphere (Finlayson-Pitts and Pitts 1986):



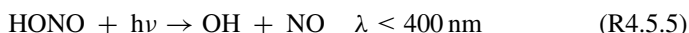
In order to make use of ozone photolysis as OH source in chamber experiments, ozone and water vapour needs to be present and UV radiation is required. Ozone

can be provided by ozone generators (Sect. 4.8). Ozonolysis reactions of unsaturated compounds may affect the chemistry of the experiment and water vapour can also affect some chemical reactions. This needs to be considered in the evaluation of experiments. If experiments need to be done in dry air, hydrogen could be used instead of water vapour. This leads to the production of equal concentrations of OH and hydroperoxy radicals:



4.5.2 OH Production from Nitrous Acid Photolysis

Nitrous acid (HONO) is commonly used as an OH source in chambers. It photolyses in the near UV–visible spectral range:



This reaction produces concurrently OH and NO that affect the radical system (Sect. 4.5.7). HONO is reformed in the reaction of OH and NO, so that both are in a photo-stationary state. The reaction of HONO with OH is a sink for OH that may compete with the reaction of OH with the target species for exceptionally high HONO concentrations:



Due to the fast photolysis of HONO (lifetime in the range of several 10 min for atmospheric conditions), typically a continuous source of HONO is required to sustain the production of OH radicals during the experiment.

Nitrous acid is not commercially available. It can be synthesized by following the protocol adapted from Nash et al. (1968), Cox et al. (1974) and Burkholder et al. (1992). HONO is generated by the reaction of an aqueous solution of NaNO_2 with diluted sulfuric acid. For example, a diluted NaNO_2 solution (0.1–1%) is continuously added to a solution of sulfuric acid (30% by weight) with a flow rate of 0.24 ml/min. The reaction can be achieved in a closed 3-necked bulb that is continuously stirred by a magnetic stirrer (Fig. 4.3). The output needs to be directly flushed into the chamber (Sect. 4.2), because nitrous acid easily decomposes. Decomposition can be minimized, if the reaction is performed in the dark and at low temperature (e.g. in an ice bath). Traces of NO, NO_2 and H_2O formed by the self-reaction of HONO can be present in the resulting mixture (Chan et al. 1976). For example, the system

Fig. 4.3 HONO generation system at EUPHORE



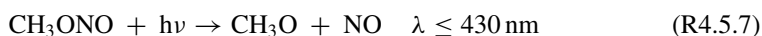
installed at the EUPHORE chamber delivers a constant flow of HONO that leads to an increase of the HONO mixing ratio in the chamber (200 m^3) of $1\text{ ppbv}/\text{min}$. Similar amounts of NO and NO_2 are concurrently observed.

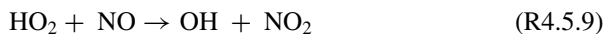
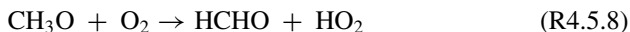
HONO is also known to be heterogeneously formed on Teflon surfaces. The exact mechanism is not fully understood. The source requires radiation and is enhanced with increasing temperature and relative humidity (Rohrer et al. 2005). Therefore, HONO is typically continuously produced in Teflon chambers that are illuminated for photochemistry experiments and can serve as OH source. Emission rates scale also with the size of the chamber. Therefore, careful characterization of the HONO source needs to be done in Teflon chambers that are used for photochemical experiments.

The HONO concentrations can be measured by LOPAP instruments (Kleffmann et al. 2002) with high precision and accuracy. Recently, also cavity-based absorption spectroscopy has been applied for the detection of HONO, but the sensitivity of these instruments is less compared to that of LOPAP instruments (Min et al. 2016). The HONO source can also be characterized in reference experiments (Chap. 2), if the increase of the total reactive nitrogen oxide concentration (NO_x) is observed assuming that HONO is the only relevant source for NO_x in the chamber (Rohrer et al. 2005).

4.5.3 Production of OH from Alkyl Nitrite Photolysis

Photolysis of alkyl nitrites can be used as an OH source in chamber experiments. The most widely used precursor is methyl nitrite. Its photolysis has been extensively studied (Gray and Style 1952; Taylor et al. 1980; Niki et al. 1981; Atkinson et al. 1981):





In contrast to ozone or H_2O_2 photolysis, low energy photons are required, thus reducing the probability that other organic compounds are concurrently photolysed. However, the by-products, formaldehyde and nitric oxide, can complicate the evaluation of experiments. For example, if the formaldehyde yield from the oxidation of organic compounds is to be determined, it is recommended to use a different alkyl nitrite such as isopropyl nitrite, for which the by-product of the photolysis is acetone. It is worth noting that OH radicals are indirectly generated from the photolysis of alkyl nitrite because HO_2 radicals can be converted to OH in the reaction with NO. This implies that methyl/alkyl nitrite photolysis should be considered as a HO_x source rather than as an OH source. In addition, the effect of the presence of NO_x on the chemical system needs to be considered (Sect. 4.5.7). Injection of additional NO is recommended to accelerate the conversion of HO_2 to OH (Reaction R4.5.9) and to suppress NO_3 and O_3 in their reactions with NO.

Alkyl nitrites, which are not commercially available, can be synthesized following an experimental protocol adapted from Gray and Style (1952) and described by Taylor et al. (1980): The alkyl nitrite is prepared by dropwise addition of sulfuric acid (50%) to a mixture of the corresponding alcohol and saturated aqueous sodium nitrite (NaNO_2). The reaction is performed at ice temperature (Fig. 4.4). A stream of oxygen-free N_2 carries the reaction products through a bubbler filled with tablets of potassium hydroxide (KOH) (or with a KOH solution) to remove acids. It is further flowed through anhydrous calcium chloride (CaCl_2) to remove traces of water. Finally, the alkyl nitrite is frozen in a trap that is kept at dry ice temperature (196 K). The purity of the alkyl nitrite can be increased by fractionally distillation in the vacuum. The crystals are colourless. If they melt, a lemon-yellow liquid is obtained. Alkyl nitrite can be kept for months in a freezer at a temperature of -18°C but it is recommended to perform a distillation after having it stored for a long time to remove impurities which could have been formed by alkyl nitrite decomposition. The alkyl nitrite is then introduced into the chamber following the procedures described in Sects. 4.2 and 4.3. Because of its high volatility, injection as a liquid is not recommended, but to prepare a gaseous mixture in a glass bulb. An example of the evolution of trace gas concentrations during the photolysis of methyl nitrite in the CSA chamber at the CNRS-LISA is shown in Fig. 4.5 demonstrating that a number of different compounds are formed in the complex system.

4.5.4 Production of OH from Photolysis of Peroxides

The photolysis of hydrogen peroxide (H_2O_2) is one way to produce OH without the need for other reactants and without the chemical production of other reactive species (Calvert and Pitts 1966):

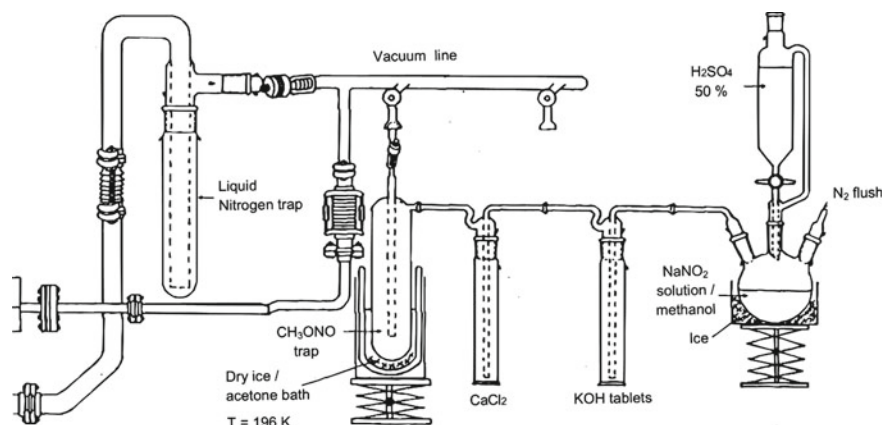
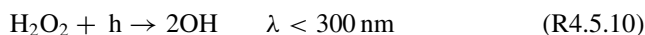


Fig. 4.4 Experimental setup for the synthesis of alkyl nitrites. (From Picquet 2000)



However, the absorption cross section of this reaction is rather small. Even at shorter wavelengths around $\lambda = 250 \text{ nm}$ the value is only approximately $8 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ and the value reduces to approximately $4 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$ at $\lambda = 350 \text{ nm}$ (IUPAC). Therefore, radiation at wavelengths $\lambda < 300$ is typically used so that photolysis of other compounds may need to be considered. In addition, high concentrations of H_2O_2 need to be injected so that the source needs to be very clean to avoid impurities affecting the experiment.

Commercial solutions of stabilized H_2O_2 with concentrations between 30 and 50% in water are often used. Higher purity solutions can be used but this requires additional purification which is dangerous as concentrated H_2O_2 solution is highly explosive. Therefore, also traces of water are concurrently injected. H_2O_2 loss at chamber wall can be significant so that the calculation of the OH production from the amount of injected H_2O_2 could lead to an overestimation of the radical source. OH concentrations can be obtained, for example, by using an OH tracer (Sect. 4.9).

The H_2O_2 solution can be introduced into the chamber by gently heating the solution, by bubbling dry nitrogen through the solution, or by direct injection with a syringe (Sect. 4.2). When bubbling a carrier gas through the H_2O_2 solution, water vapour is more efficiently taken up from the solution. As a consequence, the H_2O_2 concentrations in the solution is gradually increasing so that the H_2O_2 concentration that is transported into the chamber increases with time. Therefore, also the OH production rate in the chamber increases over time. A high concentration of H_2O_2 in the solution could become a safety problem so that caution with this method is recommended.

Radical production from the photolysis of organic peroxides can also be used as radical source in chamber experiments, but the subsequent chemistry is more complex compared to the photolysis of H_2O_2 due to the concurrent production of

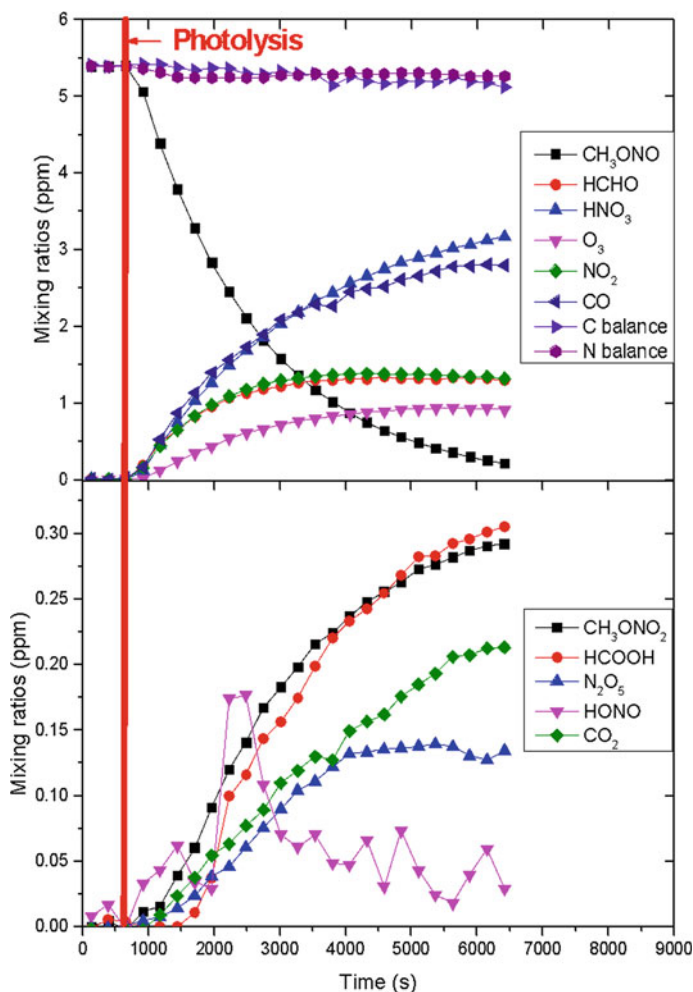
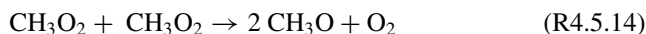
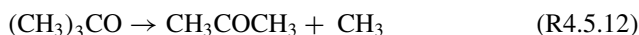
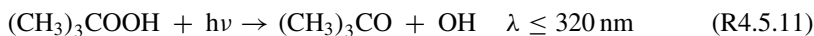


Fig. 4.5 Time profiles of reactant and products mixing ratios following irradiation of a mixture CH_3ONO in air in the CSA simulation chamber (Laboratoire Interuniversitaire des Systèmes Atmosphérique, LISA). NO is injected to enhance the conversion of HO_2 to OH (from Picquet 2000). Nitrate radicals and dinitrogen pentoxide (N_2O_5) can be formed in the experiment because NO_3 photolysis is small for the radiation of the lamps used in this experiment (wavelengths at 360 and 420 nm)

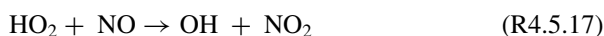
organic radicals and products. This is similar to the photolysis of alkyl nitrates, but OH is directly formed from the photolysis so that there is no need to convert peroxy radicals to OH in the reaction with NO . For example, photolysis of tert-butyl hydroperoxide proceeds by the following reactions (Calvert and Pitts 1966; Baasandorj et al. 2010):



In this case, acetone, formaldehyde, HO_2 and organic radicals are formed. Advantages of using tert-butyl hydroperoxide instead of H_2O_2 are that it is available at higher concentrations and its wall loss rate could be lower than that of H_2O_2 . Handling and injection methods are the same as for H_2O_2 .

4.5.5 Thermal Decomposition of Pernitric Acid

The thermal decomposition of pernitric acid HO_2NO_2 leads to the formation of hydroperoxyl radicals that can be further converted to OH in presence of NO (Barnes et al. 1982). In contrast to the methods described above, radicals can be produced in the dark:



As shown by Graham et al. (1977, 1978), the unimolecular decay time of HO_2NO_2 at room temperature and atmospheric pressure is on the order of 10 s. However, because a thermal equilibrium is rapidly established, the effective lifetime can be on the order of hours. It is mainly determined by the loss rate of HO_x radicals in the chemical system because the depletion of the HO_2 concentration prevents the back-reaction of HO_2 with NO_2 to HO_2NO_2 .

HO_2NO_2 can be synthesized following a protocol described by Barnes et al. (1982). Pernitric acid is prepared by reacting concentrated H_2O_2 (85%) with NO under vacuum. Typically, a 1 L glass flask containing 50 ml H_2O_2 at 0 °C is evacuated to 1 hPa. The flask is then pressurized to 400 hPa with NO while the H_2O_2 is magnetically stirred. Due to the production of HO_2NO_2 , the pressure rapidly decreases. After a few minutes, the pressure is approximately 70 hPa and the excess

of NO can be pumped out. The procedure of filling the flask with NO is repeated several times.

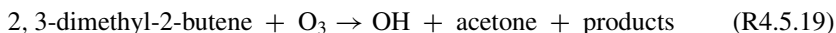
HO₂NO₂ can be injected into the chamber or gas mixtures can be prepared as described above. Because HO₂NO₂ is unstable, impurities such as HNO₃, H₂O and NO₂ are difficult to avoid and may need to be considered in the interpretation of results.

4.5.6 OH Production from the Ozonolysis of Alkenes

Another method to produce OH radicals in the dark is the ozonolysis of alkenes that is also a significant radical source in the atmosphere (Johnson and Marston 2008). The complex reaction of ozone with alkenes leads to the formation of Criegee intermediates that can stabilize or rapidly decompose to radicals with the yield Π :



In the case of 2,3-dimethyl-2-butene, the OH yield is high with a value of 0.93 ± 0.14 (Cox et al. 2020). Besides the high OH yield, its symmetric structure leads to the formation of a limited number of other products, which reduces the likelihood for interferences in the experiment:



2,3-dimethyl-2-butene is a liquid at room temperature and can therefore be injected into the chamber as described above (Sect. 4.3). Ozone generation and injection is described in Sect. 4.8.

Due to the complexity of the ozonolysis reaction that is often only partly known in detail and the concurrent production of organic radicals and organic products that can be involved in the chemical system and particle formation the interpretation of experiments can be difficult. If ozone is the limiting reactant in the system, subsequent ozonolysis reactions could be partly avoided.

4.5.7 OH Production in the Presence of NO_x

Most of the methods to produce OH radicals require radiation and nitrogen oxides (NO_x = NO₂ + NO) in the presence or absence of ozone. The reaction of OH with organic compounds initiates a radical reaction chain, in which different radical reactions compete. Depending on the availability of reaction partners, different reaction pathways can dominate the chemical system. In addition, radiation used for the initial OH production could photolyse other compounds than the OH precursor. For

example, nitrogen dioxide is often concurrently photolysed leading to the formation of ozone and nitric oxide (NO). Due to the fast back-reaction of NO with ozone, NO, O₃ and NO₂ concentrations form a photo-stationary state.

NO is also a reaction partner for peroxy radicals that are produced in the OH radical chain. The ozone that is produced from the subsequent photolysis of NO₂ leads a net increase of the ozone concentration, because no ozone has been consumed in oxidation of NO before. Therefore, also the ratio of NO₂/NO concentrations has the tendency to increase over the course of an experiment. Due to the strong coupling of radiation, radicals, nitrogen oxides and ozone, photochemistry experiments need to be carefully designed to ensure that the desired chemistry can be observed.

The OH concentration that is present in the experiment does not only depend on the production rate from radical precursors and the loss rate in its reaction with inorganic and organic reaction partners, but also on the rate of radical regeneration. The reaction of OH initiates a radical chain reaction. This radical reaction cycle includes reactions of nitric oxide (NO) with organic peroxy (RO₂) and hydroperoxy (HO₂) radicals and eventually reforms OH. Due to the short lifetime of radicals that range between a fraction of second and minutes, OH, HO₂ and RO₂ radical concentrations are quickly in a steady state. The presence of NO shifts the equilibrium toward OH and increases the number of OH regeneration cycles before competing reactions such as the reaction of OH + NO₂ and peroxy radical recombination reactions terminate the radical chain. Therefore, the addition of NO_x in chamber experiments is one method to enhance the oxidation rate of reactants. Due to the photo-chemical equilibrium between NO₂ and NO, this is most efficient, if the NO₂ photolysis rate is high. This can be achieved if the chamber is equipped with lamps providing the required radiation. Shifting the photo-chemical equilibrium to NO has also the advantage that the radical termination reaction of NO₂ with OH producing nitric acid is reduced. This reaction can otherwise limit the oxidation efficiency. Therefore, it is recommended to keep the NO_x (NO₂ + NO) concentration in a range that NO₂ concentrations are moderate.

Recently, the H-shift isomerization reactions of RO₂ have been recognized to be competitive with other radical reactions at atmospheric conditions. Subsequent reactions can also lead to the regeneration of radicals (Peeters et al. 2014) as well as to the production of highly oxidized molecules (HOMs) (Ehn et al. 2014).

Depending on the fate of organic peroxy radicals, different product distributions can be observed from the oxidation of organic compounds with OH. For example, if the dominant pathway is the reaction with NO, often aldehyde and carbonyl compounds are formed, whereas the reactions with HO₂ leads typically to the formation of hydroxyperoxides. In the atmosphere, recombination reactions of organic peroxy radicals are typically slower compared to its reactions with NO and HO₂. In chamber experiments, often high concentrations of OH and organic compounds are used to shorten reaction times and to accumulate measurable product concentrations, thereby increasing the production rate of RO₂ radicals. This could, however, drive the chemical regime towards RO₂ + RO₂ recombination reactions so that results may not be easily transferred to atmospheric conditions.

In experiments that aim for studying oxidation pathways that favour RO₂ + RO₂ or RO₂ + HO₂ reactions, the competing reaction with NO needs to be suppressed. This

can be achieved by injecting ozone or by using an OH source that does not concurrently produce nitrogen oxides such as H₂O₂ photolysis (Sect. 4.5.4). However, the release of HONO in chambers that are made of Teflon film may limit the minimum concentration of nitrogen oxide species (Chap. 2). If the goal of the experiment is to investigate uni-molecular hydrogen shift reactions in RO₂ radicals all, bi-molecular RO₂ reactions need to be suppressed. In addition to minimizing the NO concentration, low reactant concentrations are required to reduce the loss due to RO₂ recombination reactions. This, however, may be limited by competing chamber effects interfering with the chemical system or by the sensitivity of instruments.

4.6 Production of Nitrate Radicals

The nitrate radical (NO₃) is photochemically unstable in the presence of visible light but can accumulate in the absence of sunlight. In consequence, NO₃ acts as a night-time oxidant in the atmosphere. Studying NO₃-initiated processes in simulation chambers allows the provision of both kinetic and mechanistic data of individual reactions or entire chemical reaction systems. They are typically performed in the dark to avoid photodissociation of NO₃. Like OH, NO₃ radicals need to be generated during the experiment and the reaction of NO₃ with organic compounds can initiate a reaction chain that needs to be considered in the evaluation of experiments. Several methods have been developed to produce NO₃ including reactions of halogens with nitric acid, photolysis of nitric acid or reaction of chlorine atoms with chlorine nitrate (Wayne et al. 1991), but only few of them are suitable for chamber simulation experiments and are described in the following sections.

4.6.1 Production of NO₃ from the Gas-Phase Reaction of NO₂ and O₃

In the atmosphere, NO₃ radicals are produced from the gas-phase reaction of nitrogen dioxide and ozone. This process can be applied in chamber experiments by injecting NO₂ (Sect. 4.2) and O₃ (Sect. 4.8):

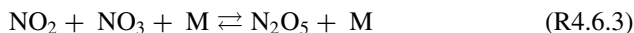


Instead of injecting NO₂, also NO can be used to produce NO₂ from its reaction with ozone:



The advantage of using NO is that the purity of NO that is commercially available can be higher compared to that of NO₂.

The reaction rate constant at room temperature is relatively low with a value of $k_{4.6.1} = 3.2 \times 10^{-17} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$. Due to the presence of NO_2 , part of the produced NO_3 is further converted to dinitrogen pentoxide (N_2O_5) that is thermally labile:



In most cases, NO_3 and N_2O_5 concentrations can be assumed to be in a thermal equilibrium.

The actual NO_3 concentration in the chamber is typically highly variable because NO_2 and O_3 required for the production are consumed and the N_2O_5 serves as a reservoir for NO_3 (Fig. 4.6). The formation of N_2O_5 can be minimized by using higher ozone than NO_2 concentrations (Mitchell et al. 1980). However, ozone itself can be an oxidant that could interfere becoming significant for the evaluation of the experiment if high ozone concentrations are present.

The loss rate of NO_3 due to oxidation of reactants in chamber experiments is typically much lower compared to that of the OH radical. Therefore, chamber wall loss reactions can compete and contribute significantly to the total loss of NO_3 in the experiments even in chambers with a large volume-to-surface ratio (Fig. 4.6, Dorn

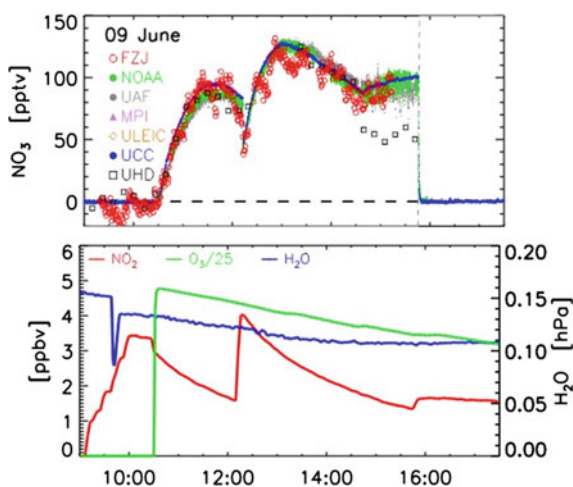


Fig. 4.6 NO_3 formation from the reaction of NO_2 and O_3 in the SAPHIR simulation chamber in Jülich, Germany, during the NO_3 radical intercomparison campaign. O_3 was injected once and NO_2 several times over the course of the experiment to enhance the production rate of NO_3 . Despite its large volume of 270 m^3 , NO_3 wall loss is significant so that the NO_3 concentration reaches maximum concentrations approximately 1 h after the last injection of reactant. Shortly before 16:00 the air mixture was exposed to sunlight leading to the rapid destruction of NO_3 . (Reused with permission from Dorn et al. (2013) Open access under a CC BY 3.0 license, <https://creativecommons.org/licenses/by/3.0/>)

et al. 2013). In addition, N_2O_5 wall loss could impact the chemical system due to its thermal equilibrium with NO_3 .

NO_3 radicals can also be formed in a reactor outside the chamber and the air mixture can be flushed into the chamber (Thuener et al. 2004). Concentrations can be chosen, such that one of the reactants, NO_2 or O_3 , is in excess, whereas the other reactant is consumed in the reactor so that NO_3 production stops before the air mixture enters the chamber. The reaction time that would be required to consume both reactants would be much longer than the NO_3 lifetime in the reactor with respect to wall loss. If ozone is consumed in the reactor, this method allows for experiments without additional ozonolysis reactions. The reactor needs to be kept in the dark and it is recommended to use inert materials such as Teflon or SilcoTec® coated steel.

Because of the complex chemical system and the impact of wall loss, trace gas concentrations should be monitored. The detection of NO_2 and O_3 belongs typically to the standard repertoire of measurements with commercial instruments at chambers. The measurement of NO_2 and O_3 allows calculating the production rate of NO_3 . The direct detection of NO_3 is typically done with custom-built instruments applying absorption spectroscopy (Dorn et al. 2013) but can be challenging due to its high reactivity and small concentrations. Detection of less reactive N_2O_5 by FTIR or cavity-based absorption spectroscopy can be used to calculate NO_3 concentrations from the thermal equilibrium between NO_3 and N_2O_5 (Reaction R4.6.3), if the NO_2 concentration and temperature are monitored in the experiment.

4.6.2 Production of NO_3 from the Thermal Decomposition of N_2O_5

N_2O_5 can be frozen as crystals at dry ice temperature. Therefore, NO_3 can be delivered to the chamber by first producing and storing frozen N_2O_5 and then injecting it into the chamber as described for solid compounds by flowing an air stream over the frozen crystal (Sect. 4.4). The evaporation rate can be controlled if the temperature of the cold trap containing the crystals can be varied.

While the air is heating up to the temperature in the chamber, NO_3 and NO_2 are produced from the thermal decomposition of N_2O_5 that has evaporated from the crystal (Reaction R4.6.3, Fig. 4.7). Therefore, this method provides ozone-free NO_3 (Atkinson et al. 1984a, b; Barnes et al. 1990; D'Anna et al. 2001; Spittler et al. 2006; Kerdouci et al. 2012; Slade et al. 2017). However, NO_2 is a by-product of the N_2O_5 decomposition. One challenge is to minimize impurities because the solid sample can contain other nitrogen oxide compounds present in the synthesis such as NO_2 and nitric acid.

N_2O_5 can be synthesized from the gas phase reaction of NO_2 and O_3 (Reactions R4.6.1 and R4.6.3) in a vacuum line and two glass traps (Fig. 4.7). N_2O_5 freezes out, if the gas mixture is flowed through a glass trap that is kept in a dry ice or a mixture of liquid nitrogen/ethanol bath. The temperature of the trap should be around 193 K

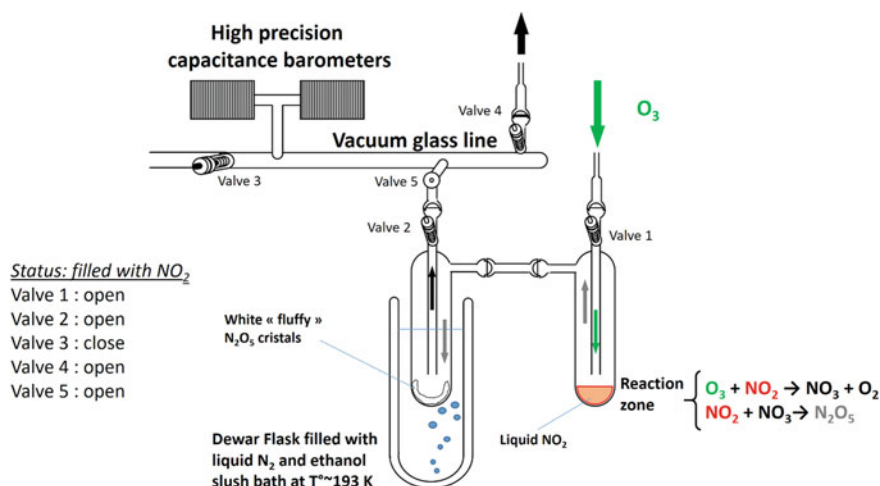


Fig. 4.7 Set-up for producing frozen N_2O_5 crystals using a vacuum preparation line

and must not be less than 163 K to avoid condensation of ozone. Instead of using liquid nitrogen/ethanol, also dry ice and an alcohol can be used to achieve a similar temperature.

In order to minimize impurities in the frozen sample, the following procedure is recommended:

- The entire vacuum line and traps should be cleaned to remove any traces of impurities and adsorbed water from the surfaces. As an anhydride, N_2O_5 reacts rapidly with water to form nitric acid. The traps are recommended to be dried in an oven for several hours. The vacuum with the two attached traps (Fig. 4.7) can be flushed with dry nitrogen and then pumped down to low pressure (10^{-3} hPa) for several hours.
- A Dewar flask containing a mixture of liquid nitrogen and ethanol at approximately 193 K is prepared and the first trap is cooled down. After closing the connection of the traps to the vacuum line the trap is filled with NO_2 (several hundred hPa) so that NO_2 condenses as white crystals. This procedure can be repeated several times to accumulate a sufficiently high amount of frozen NO_2 .
- The Dewar flask is then moved to the other trap, NO_2 slowly warms up and turns into a brown liquid and while ozone is flowed through the two traps. This is done at atmospheric pressure (Fig. 4.7). NO_2 that evaporates in the first trap reacts with ozone to form NO_3 and N_2O_5 that freezes out in the second trap. High ozone concentrations are required that can be produced with a silent discharge ozoniser fed with pure oxygen (Sect. 4.8). The total flow rate is recommended to be between 1.5 and 2 l/min so that the residential time in the trap is long enough to allow N_2O_5 to freeze as fluffy white crystals. All NO_2 must have been consumed before entering the second trap to prevent from NO_2 being frozen again

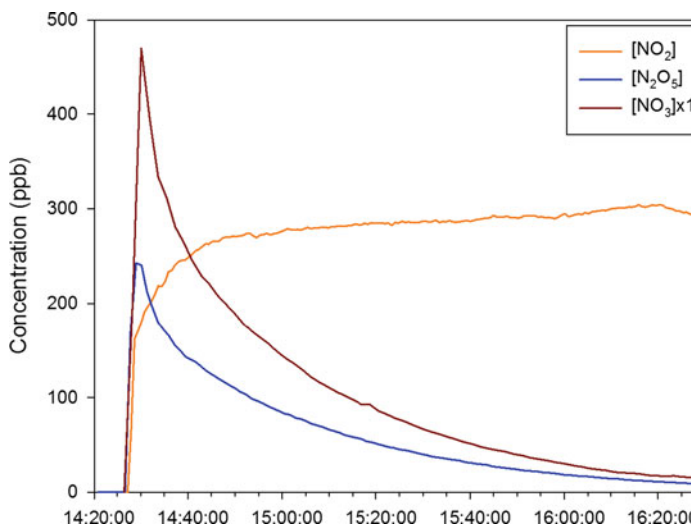


Fig. 4.8 Time series of N_2O_5 , NO_3 and NO_2 after the injection of N_2O_5 from evaporating frozen N_2O_5 in the CSA simulation chamber at LISA-CNRS (©). NO_3 and NO_2 are produced from the thermal decomposition of N_2O_5 . NO_3 and N_2O_5 concentrations are decreasing due to chamber wall loss (Fouqueau 2019)

in entering the second trap. This can be checked by the change of the gas colour from yellow/brown to colourless.

- The N_2O_5 crystals can be further purified by pumping on the bulb containing them, by removing the Dewar flask and connecting it to the vacuum pump. Under reduced pressure, as N_2O_5 has a much lower vapour pressure than NO_2 , impurities are eliminated from the crystals that are formed. N_2O_5 crystals can be stored under vacuum at a temperature of $-18\text{ }^\circ\text{C}$ for several weeks.

The injection of NO_3 from frozen N_2O_5 method is, for example, applied in the CSA and CESAM atmospheric simulation chambers at Laboratoire Interuniversitaire des Systèmes Atmosphérique (LISA). As an example, Fig. 4.8 shows the time series of trace gases after injections of N_2O_5 at the start of the experiment. Significant wall loss leads to the consumption of N_2O_5 and NO_3 .

4.7 Production of Cl Radicals

In the atmosphere, chlorine atoms are homogeneously formed from the photooxidation of chlorine compounds or from heterogeneous processes occurring, for example, on sea salt particles (Simpson et al. 2015). In chamber experiments, the production of chlorine atoms is based on the photolysis of various precursors, organic or inorganic halogenated species that are injected following the procedures described in Sects.

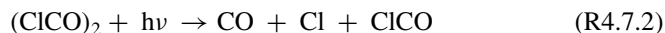
4.2–4.4. The photolysis of the precursor should have a large quantum yield at the wavelength of the radiation that is provided in the chamber. Neither the precursor nor products from the photolysis other than chlorine should interfere with the reaction system that is investigated. The photolysis of a precursor should have a large quantum yield for the available radiation and experiments should not be affected by by-products.

The most common source for Cl atoms is the photolysis of gaseous Cl₂ in air at wavelengths of $\lambda > 300$ nm. This reaction produces only Cl atoms (Atkinson and Aschmann 1985):



Photolysis of compounds other than Cl₂ that are present in the chamber experiment may need to be considered, but most organic compounds do not photolyse at these wavelengths. Cl₂ can be injected into the chamber as described in Sect. 4.2. Although a clean source, Cl₂ is prone to react directly with unsaturated species and sulphur compounds. Molecular chlorine is also a harmful gas and proper safety measures must be taken when handling it.

There are several other precursors that require radiation at lower wavelengths than Cl₂ to produce chlorine atoms from photolysis such as phosgene (COCl₂, carbonyl dichloride), 2,2,2-trichloroacetyl chloride (CCl₃COCl, Hass et al. 2020), chloroform and tetrachloro methane (Matheson et al., 1982). Among these, oxalyl chloride is most commonly used (Baklanov and Krasnoperoy 2001; Gosh et al. 2012):



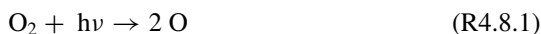
The photolysis of oxalyl chloride is a relatively clean source for chlorine atoms, because the only by-product is CO. It is commercially available as a liquid and does not require special safety measures. Oxalyl chloride can be injected into the reaction chamber following the procedures described in Sect. 4.3 by either direct injection with a syringe or by flowing dry air through a heated Pyrex glass bulb containing the liquid oxalyl chloride. If high energy-rich radiation is applied, the photolysis of organic compounds may need to be considered in the evaluation of experiments.

4.8 Production of Ozone

Ozone (O₃) plays an important role in tropospheric chemistry. Its photolysis is the most important source of OH radicals (Sect. 4.5.1) and it is an oxidant for organic compounds (Sect. 4.5.6). Ozone can be stored at low temperature as a solid, a liquid or can be adsorbed; however, storing ozone is not recommended due to the difficult handling and serious safety issues. Therefore, gaseous ozone is directly produced before injecting it into the chamber.

4.8.1 Photochemical Ozone Generation

Ozone can be generated by using an ultraviolet lamp emitting radiation at a wavelength of 185 nm (Fig. 4.9). Low-pressure discharge mercury lamps such as “pen ray Hg lamps” are often used. Their main emission line is at a wavelength of 254 nm, but they also emit 185 nm radiation to dissociate oxygen:



Pure oxygen or synthetic air is flowed through a glass bulb that is illuminated by the lamp. The lamp can be placed outside if the bulb is made of fused quartz glass. Shielding of all radiation including any stray light is required for safety reasons due to the high potential for damages of DNA, if the radiation hits the skin of humans. It is highly recommended to have all parts of the system made of glass or Teflon to avoid rapid destruction of ozone on surfaces.

The resulting ozone concentration highly depends on the residence time of the air in the photoreactive region, on the pressure, and on the lamp emission power and needs to be characterized for each design of a device. The maximum ozone production is mainly limited by the size of lamps and glass bulbs. For example, the device used at the EUPHORE chamber produces 23ppbv of ozone per min in a volume of 200m³.

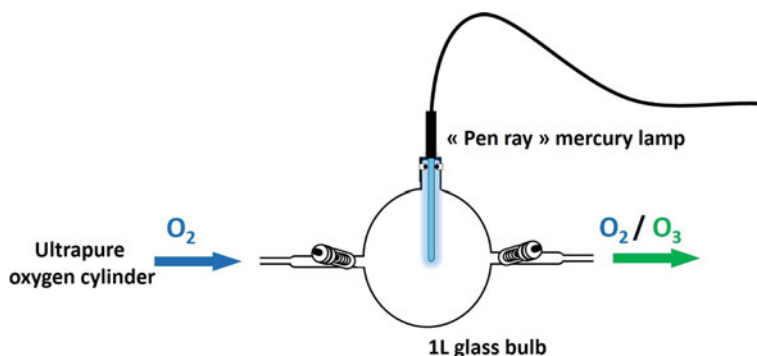


Fig. 4.9 Example of a photolytic ozone generation set-up

4.8.2 Ozone Generation by Electrical Discharge

Ozone can also be generated with ozone discharge generators that are commercially available. They provide a reproducible ozone production rate and have a high efficiency so that ozone mixing ratios in the percentage range in the output gas flow can be achieved. They are based on dissociating oxygen in an electric field. It is important to use high-purity oxygen to avoid artefacts from the concurrent dissociation or recombination reactions of other compounds or impurities. For example, using air containing nitrogen in addition to oxygen leads to the production of high concentrations of complex nitrogen oxides.

Some devices use a high-voltage electric arc between two electrodes, but they are not recommended because particles can be released from the surfaces of the electrode that are flushed into the chamber together with the ozone. Instead, “silent discharge” or “corona” ozone generators should be used. They produce a plasma between two dielectric electrodes. In a corona discharge ozone generator, the electrical discharge takes place in an air gap within the corona cell designed specifically to split the oxygen molecule for the ozone production. In this air gap, a dielectric is used to distribute the electron flow evenly across the gap (Gibalov and Pietsche 2006). These generators are not only very efficient, but they are also very robust which makes their use convenient for simulation chamber experiments.

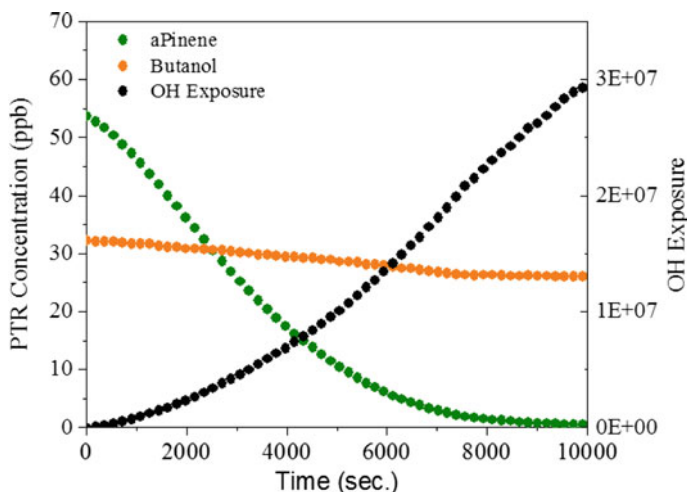


Fig. 4.10 OH exposure calculated from the measured time series of the butanol concentration in the 8 m³ chamber at Paul Scherrer Institute during an experiment in which α -pinene is oxidized

4.9 Using OH Radical Tracers in Simulation Experiments

OH radical initiated chemistry is extensively used in atmospheric simulation chambers to study both gas-phase chemistry and SOA formation. However, because of its fast reaction rates, the OH radical is present only in low concentrations making its direct detection difficult. Typically, Laser Induced Fluorescence (LIF), Differential Optical Laser Absorption Spectroscopy (DOAS) or Chemical Ionization Mass Spectrometers (CIMS) instruments are used to measure OH radicals in the atmosphere or in an atmospheric simulation chamber (Schlosser et al. 2009). However, not all chambers have access to such an instrument to provide a direct measure of OH radicals. Therefore, having a robust method by which to infer OH radical concentration with typical chamber instrumentation is important to constrain processes occurring in the chamber and to be able to connect data obtained from atmospheric simulation chambers to the ambient atmosphere. Without having a measure of OH exposure, variations between experiments can easily be attributed to different processes when in reality only the formation or destruction of OH radicals have changed. This is especially necessary in cases of complex emissions where reproducibility of experiments can be difficult to achieve.

One way to track the OH concentrations during an experiment is to add an additional organic compound to the chamber that has an established OH reaction rate and to follow its decay throughout an experiment. This method was demonstrated by Atkinson et al., where they calculated the yields of formation of OH radicals from the ozonolysis of various terpenes (Atkinson et al. 1992). Yields of OH radicals were inferred by monitoring the products of an OH scavenger (for example, cyclohexanone and cyclohexanol from the reaction of OH with cyclohexane) as measured by a gas chromatography coupled with a flame ionization detection (Atkinson et al. 1992; Alam et al. 2011).

Another method that has been applied is the use of 1,3,5-trimethyl benzene (TMB) as a tracer molecule of OH radicals during chamber studies (Rickard et al. 1999). However, a downside to using TMB is the high potential for forming SOA, making it non-ideal for studies aiming at studying SOA since the tracer will be incorporated into the aerosol. This would suggest that smaller molecules would be better tracers for OH reactivity because they will not form SOA or be incorporated into it. Another consideration when choosing a tracer comes from possible overlap with the tracer and an oxidation product or fragment of the desired VOC. The final consideration is that the OH tracer should react sufficiently slow enough to remain in the chamber throughout the experiment and its reactivity with OH does not significantly compete with the reactivity of the target compounds.

To avoid these problems, d_9 -butanol has been used as an OH tracer (Atkinson et al. 1992; Barmet et al. 2012; Stefenelli et al. 2019). This molecule does not overlap with other molecules or fragments, if organic compounds are detected, for example, with a proton-transfer mass spectrometer (PTR) because the deuteration shifts the parent ion to an even mass, as opposed to most molecules that have an odd mass when reacting with the reagent ion (H_3O^+ in case of the PTR instrument). Oxidation products of

d_9 -butanol are small molecules that have a high vapour pressure so that they do not partition into the aerosol phase and thereby do not interfere in experiments, in which particles are investigated.

If only one tracer is used, the OH exposure that is defined as OH concentration integrated over time can be determined from the measured tracer concentration:

$$OH\ Exposure(t) = \frac{[tracer]_0 - [tracer]_t}{k_{OH, tracer}} \quad (4.9.1)$$

$k_{OH, tracer}$ is the reaction rate constant of the tracer with OH and $[tracer]_0$ is the initial tracer concentration (Fig. 4.10).

This method can be extended by using two tracers which have a significant different reaction rate constants in the reaction with OH. For instance, Stefenelli et al. (2019) chose naphthalene as a second tracer in addition to d_9 -butanol. In this case, the OH exposure can be calculated from the ratio of the measured tracer concentrations:

$$OH\ Exposure(t) = \left(\frac{\ln\left(\frac{d_9butanol}{naphthalene}\right)_0 - \ln\left(\frac{d_9butanol}{naphthalene}\right)_t}{k_{OH, butanol} - k_{OH, naphthalene}} \right) \quad (4.9.2)$$

If the tracers are lost by other processes than the reaction with OH during the experiment such as dilution, the estimated OH exposure would be too high, if these loss processes are not taken into account. In this case, loss rates (k_{loss}) of these processes need to be accurately known to correct measured concentration time series. An iterative correction procedure is, for example, described in Galloway et al. (2011):

$$[tracer]_t^{corr} = [tracer]_{t-1}^{corr} + [tracer]_t - [tracer]_{t-1} + [tracer]_{t-1} \Delta t k_{loss}$$

4.10 Using OH Scavengers in Simulation Experiments

In oxidation experiments, the coupling of different oxidants specifically in the production of OH radicals (Sect. 4.5) it is often challenging to disentangle the complexities of the chemical system in chamber experiments (Bianchi et al. 2016; Riva et al. 2019). For example, ozonolysis of alkenes produces OH radicals with yields between 0.13 and 1.15, (Rickard et al. 1999) so that the reaction of the organic compound with OH competes with the reaction with ozone in the experiment (Atkinson et al. 1992). The reaction with OH can be suppressed, if a OH scavenger is additionally injected as often done in many experiments investigating ozonolysis reactions (Docherty and Ziemann 2003; Donahue et al. 2005; Henry and Donahue 2011; Henry et al. 2012; Keywood et al. 2004). The concentration of the radical scavenger must be sufficiently high so that the majority of the OH radicals

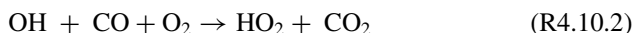
(e.g. more than 99%) react with the scavenger instead other reactants in the chemical system:

$$\frac{k_{OH+scavenger}[scavenger]}{k_{OH+scavenger}[scavenger] + k_{OH+reactant}[reactant]} > 0.99 \quad (4.10.1)$$

Typically, it is sufficient to calculate the amount of scavenger that is required for the maximum concentration of the reactant, because the OH production rate, for example, from the ozonolysis of the reactant is expected to decrease while the reactant concentration is decreasing (Fig. 4.11). In some cases, also OH production from product species may need to be additionally considered.

The chemistry from the OH scavenger and from the products of its reaction with OH needs to be taken into account in the evaluation of experiments. It should not significantly interfere with the chemical system that is investigated in the experiment.

CO is often used as scavenger in ozonolysis studies because it is unreactive to ozone. The reaction with OH generates HO₂ and CO₂:



Typical other OH scavenger molecules are H₂, H₂O₂, and organic compounds such as alcohols, and alkanes.

There are no organic compounds produced from the reaction of the scavenger with OH, if CO, H₂ or H₂O₂ are used so that experiments are not affected by organic

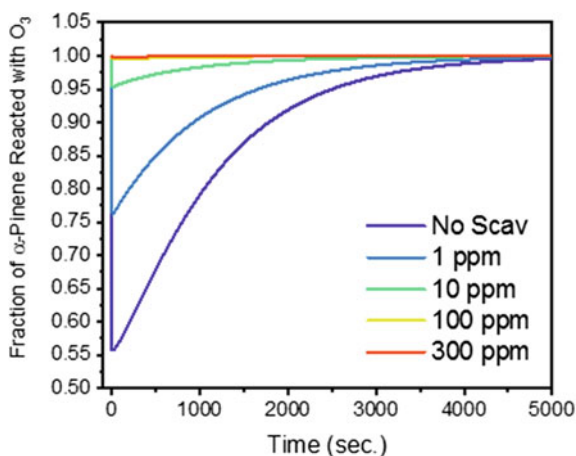


Fig. 4.11 Model calculations showing the effect of the injection of 1-butanol as OH scavenger in an experiment, in which the ozonolysis ($[O_3]_0 = 500$ ppbv) of α -pinene (100 ppbv) is investigated, on the temporal evolution of the fraction of α -pinene that reacts with ozone. Without scavenger, the fraction of OH reaction can be as high as 45%, whereas 300 ppmv 1-butanol is sufficient to scavenge all OH radicals so that the reaction of α -pinene with OH is suppressed

compounds produced from the scavenger. However, the reaction rate constants of their reactions with OH is relatively low so that large concentrations of the scavenger are required. This can cause safety hazards, because H_2 and CO are inflammable gases and CO is toxic.

An interference from H_2O_2 can occur in experiments investigating the aerosol phase, because H_2O_2 can be taken up on particles specifically at elevated relative humidity. Further impact from the scavenger molecules on the experiment can be caused by the radicals that are produced in their reaction with OH, because they take part in the radical reaction system in the experiment. Depending on the production rate of OH, significant concentrations of peroxy radicals can be produced.

The reaction of CO, H_2 and H_2O_2 with OH leads to the production of HO_2 (Reaction R4.10.2) so that HO_2 concentrations can be significantly higher compared to an experiment without scavenger (Fig. 4.12). This can shorten the lifetime of RO_2 radicals formed from the ozonolysis of organic compound due to their reaction with RO_2 and could potentially alter the product distribution (Keyword et al. 2004).

If an organic compound is used as OH scavenger, the impact of organic compounds needs to be considered. In addition, RO_2 formed from the scavenger could also affect the chemical system by increasing the rate of radical recombination reactions. Recent studies have also shown that the presence of RO_2 radicals formed from the scavenger + OH reaction pathway can result in the formation of dimers that include RO_2 derived from the scavenger. Therefore, the scavenger may also impact the formation of secondary organic aerosol (McFiggans et al. 2019; Zhao et al. 2018).

In general, it is recommended to perform sensitivity model calculations to estimate the impact of an OH scavenger on the results of the experiment.

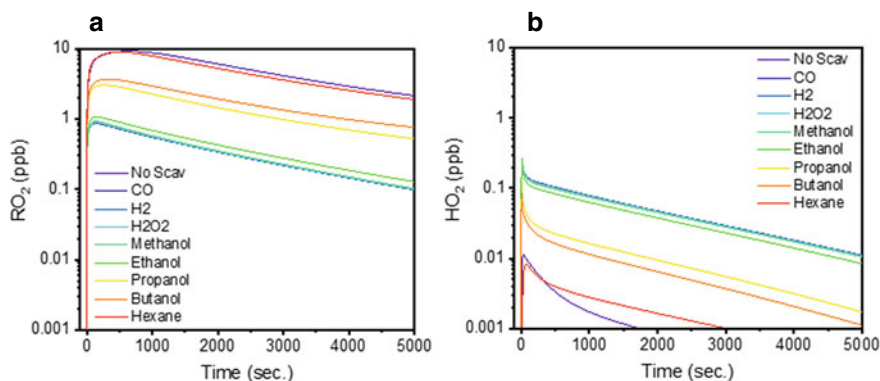


Fig. 4.12 Concentrations expected from model calculations using MCM 3.3.1 for RO_2 (a) and HO_2 (b) radicals during the ozonolysis of α -pinene in a chamber experiment for a mixture of α -pinene (100 ppbv), O_3 (500 ppbv). Model calculations are performed for different OH scavenger molecules (CO–30,000 ppmv, H_2 –2%, H_2O_2 –500 ppmv, methanol–500 ppmv, ethanol–500 ppmv, propanol–500 ppmv, butanol–300 ppm, and hexane) demonstrating the effect on radical concentrations in the chamber experiment

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