

## OH Kinetics

Reactions were carried out at  $295 \pm 2$  K and atmospheric pressure in a collapsible pillow-shaped fluorine-ethene-propene (FEP) Teflon reaction chamber, shown in Figure 2.2. The FEP foil is highly resistant to chemical attack and shows high transparency in the visible and UV regions of the electromagnetic spectrum. The reactor is operated using purified air which contains very low levels of non-methane-hydrocarbons ( $< 10$  ppbV),  $\text{NO}_x$  ( $< 10$  ppbV) and water.

The approximate capacity of the reactor is 250 litres of air at atmospheric pressure. Four apertures sealed into the foil were used for the introduction and sampling of gases and vapours. The reactor is surrounded by 8 lamps with  $\lambda_{\text{max}} = 350$  nm (Philips TL05) and 4 lamps with  $\lambda_{\text{max}} = 254$  nm (Philips TUV) arranged on four different circuits which allow variation of light intensity and wavelength. The FEP foil transmission and lamp emission characteristics can be seen in Figure 2.3. The reactor is coupled to a gas chromatograph for chemical analysis.

Prior to addition of reactants the chamber was filled with 200 litres of purified air using a flow meter at a rate of  $20 \text{ L min}^{-1}$  for 10 minutes. A gas chromatogram of the contents was then taken to ensure that no impurities were in the chamber. Addition of reactants to the chamber was carried out using a glass impinger. The reactants were individually injected into the impinger using a  $50 \mu\text{L}$  syringe. Concentrations ranging from 20 to 40 ppmV of reactant and reference compounds were used during the experiments. In each experiment, the initial concentrations of substrate and reference compounds were established to provide ratios of approximately 1:1, 1:2 and 2:1 as this range was expected to highlight the possibility that secondary reactions could also be contributing to the loss of reactants. While gently heating the base of the impinger with a hot air gun, purified air from the air purification system was used to flush the reactants into the chamber through the Teflon tubing. The contents of the chamber were then left for approximately one hour to ensure uniform mixing. A homogeneous reaction mixture was confirmed by reproducible gas chromatographic analysis.

Photolysis of methyl nitrite was used as the OH source. Methyl nitrite was added to the reactor through the vacuum line. Measured amounts of methyl nitrite were flushed from a calibrated pyrex bulb of known volume (579 mL) into the chamber by a stream of purified air. A gas chromatogram of the contents was taken to confirm the presence of CH<sub>3</sub>ONO. The reactant mixtures were photolysed (3 TL05 lamps) for 2-3 minutes and a gas chromatogram of the chamber contents was taken. This photolysis-sampling procedure was repeated until around 30% depletion of the substrate and reference compound was achieved; any further depletion may give rise to complications from the presence of reaction products. Typically 6-9 photolysis-sampling steps were carried out during each experiment. At least three experiments were carried out with each compound.

Before kinetic experiments were carried out, the possibility of wall loss and photolysis of the aldehydes and reference compounds were investigated. To check for wall loss, compounds were left in the chamber for up to five hours. Gas chromatographic analysis was performed at approximately 8 minute intervals to observe any loss of compounds to the walls of the reactor over time. Irradiation in the absence of radical precursor was carried out to ascertain the photostability of reactants. The TL05 lights were switched on for the same amount of time as in a relative rate experiment. In the gas chromatographic analysis of relative rate experiments, tests were carried out for possible overlapping retention times of reactants and irradiation products. These involved experiments in which mixtures of CH<sub>3</sub>ONO / substrate and CH<sub>3</sub>ONO / reference compound were irradiated separately and analysed.