Peroxy radical photolysis in the near UV
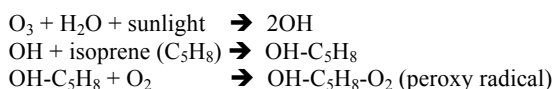
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Introduction

Atmospheric chemical models capture many of the important processes required to make reliable predictions of the hydroxyl radical (OH), the major oxidant in the troposphere removing the majority of trace gases. For pristine forested environments, e.g. in Amazonia [1] and Borneo, [2] the chemistry is dominated by isoprene oxidation under low NO_x conditions (and with relatively low $[O_3]$ limiting primary OH production), which in principle simplifies the chemistry:

$$O_3 + H_2O + sunlight \ ➔ \ 2OH$$
$$OH + isoprene \ (C_5H_8) \ ➔ \ OH\text{-}C_5H_8$$
$$OH\text{-}C_5H_8 + O_2 \ ➔ \ OH\text{-}C_5H_8\text{-}O_2 \ (peroxy \ radical)$$

but the measured [OH] is still much higher than is modelled, by up to an order of magnitude. Chemical mechanisms have been proposed where OH is generated directly from isoprene derived peroxy radicals [3]

$$OH\text{-}C_5H_8\text{-}O_2 \ ➔ \ OH \ (too \ slow)$$
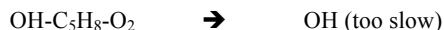
but recent experiments indicate this chemistry is an inadequate source of OH.[4] OH radicals in these regions are responsible for the destruction of much of the methane, an important greenhouse gas in the atmosphere, and therefore an understanding of OH chemistry is vitally important to predict future climates.

We have postulated that a significant fraction of the missing OH source is not unknown chemistry but is due to peroxy radical photolysis:

$$OH\text{-}C_5H_8\text{-}O_2 + hv \ ➔ \ OH$$
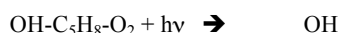
However, little or nothing is known about the photolysis of peroxy radicals, especially the yield to produce OH. This process will only be atmospherically significant if it is occurring above 300 nm, the atmospheric window.

In this work the photolysis of peroxy radicals (RO_2) to produce OH is investigated in the near UV, 300 – 350 nm, using the laser loan pool YAG / dye laser (**NSL2 system)** to do the variable wavelength peroxy radical photolysis, and another dye laser is used to monitor the resulting OH via laser-induced-fluorescence, the FAGE laser. The peroxy radical can be produced either with another photolysis laser, see Figure 1b, or made continuously using an Hg lamp in a reactor situated before the pinhole of the Fluorescence by Gas Expansion (FAGE) cell, Figure 1a.

Experimental

In the study we have investigated the setup in Figure 1a as an alternative method to the setup in Figure 1b. The FAGE method to detect OH is so highly sensitive that it is used in field measurement to measure the very small amounts of OH present in the atmosphere, 10^6 molecule cm^{-3} is typical. [5] Therefore it should offer advantages.
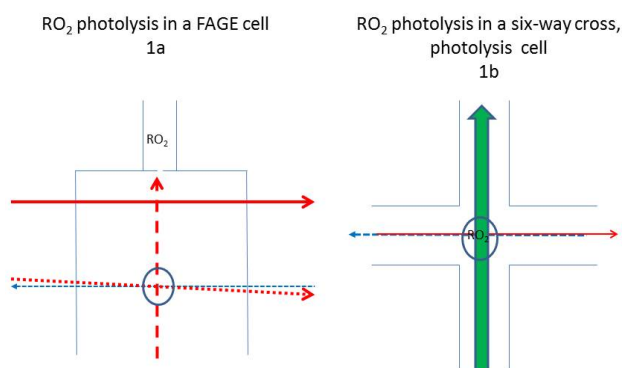
Figure 1a: Low pressure FAGE cell (~2 Torr) to do laser induced fluorescence (blue line). The red lines are the three photolysis geometries. RO_2 radicals are continuous made using an Hg lamp situated before the pinhole. After the pinhole, the RO_2 radicals flow towards the fluorescence imaging zone, circle. **Figure 1b**: Flash photolysis (green) is used to generate RO_2 radicals. The RO_2 radicals are photolysed (red) with a second laser and the OH is detected via fluorescence from the third laser (blue). All three laser beams cross in the fluorescence imaging zone, circle.

Known flows of N_2/O_2 were bubbled through water into the reactor (~400 Torr) where the Hg lamp photolysed H_2O vapour (185 nm output):

$$H_2O + hv(185 \ nm) ➔ \ OH \ + \ H$$
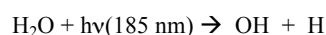
The OH then reacted with the alkene – ethylene and isoprene, see scheme above – to generate the peroxy radical, where the alkene was flowed in the reactor after the lamp to avoid photolysis. It is estimated that the concentration of the peroxy radical was $\sim 10^{11}$ molecule cm^{-3}. These peroxy radicals entered the FAGE cell via the 1 mm pinhole, where three dye laser photolysis geometries were evaluated, see Figure 1a. The OH generated from RO_2 photolysis were detected by the 5000 Hz FAGE laser. This signal was detected by the photomultiplier and digitized by the multichannel scaler. The 10 Hz output of the RO_2 photolysis dye laser was typically 10 mJ and was tuneable over the wavelength range 310 – 330 nm. The duration of each experiment was typically 1000 – 5000 pulses of the UV photolysis laser. The gas flow from the reactor into the FAGE cell was ~ 3.5 l/min and implies that it takes a few milliseconds to reach the imaging zone from the pinhole. Therefore the FAGE laser potentially samples photolytically generated OH several times (only for geometries 1 and 2, see Figure 2) before the OH has flowed beyond the imaging zone.
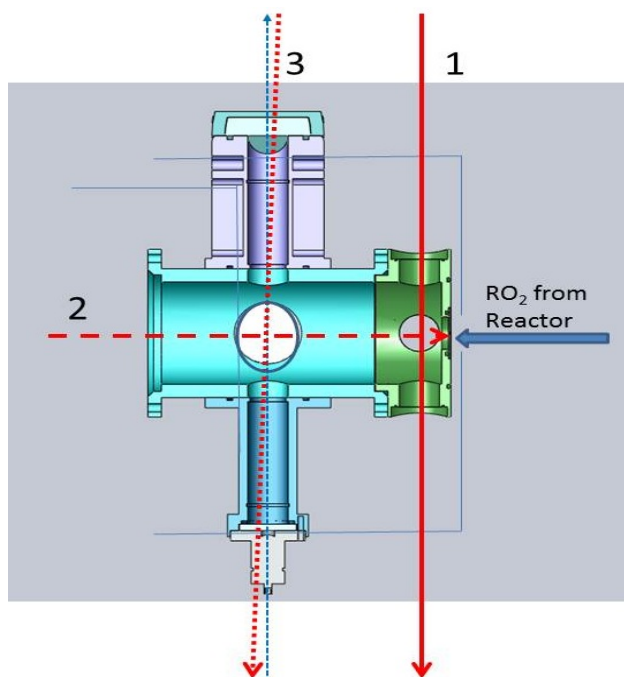
Figure 2. A solid model drawing of the FAGE cell. RO_2 radicals flow through the pinhole and are photolysed using the three (red) geometries before OH is detected via the second laser, (blue).

Results

Geometry 1

The first photolysis geometry (solid red line, Figure 2) irradiated the peroxy radical approximately 1 cm from the pinhole. The detected OH was only a few counts per 5000 shots, and was essentially close to the detection limit. It indicates that this geometry is sampling the low pressure region beyond the high density supersonic jet and only a fraction of the OH from photolysed RO_2 radicals reach the imaging zone of the FAGE cell. Based on the signals from the other geometries it is estimated only ~ 0.02 of the OH reaches the imaging zone.

Geometry 2

The second photolysis geometry (long dashed line, Figure 2) irradiated the peroxy radical perpendicular to the OH FAGE laser and crossing the imaging zone before hitting the pinhole. An extremely large signal was observed that persisted for milliseconds, see Figure 3, top. However, only the small, first point is from RO_2 photolysis. The extremely large signal after the first time point scaled non-linearly with dye laser energy and was much reduced when the metal pinhole was swapped for a glass pinhole. This evidence is consistent with the OH signal originating from a multi-photon process where the dye laser hits the pinhole. Turning off the Hg lamp or the flow of alkene only affected the signal of the first point. Attempts to subtract on and off experiments to observe more than one RO_2 photolysis points were unsuccessful; two extremely large numbers have too much noise associated with it.

A few experiments were carried out where the pinhole was removed so that the pressure of the RO_2 reactor and the FAGE cell were equal. However, it proved difficult to completely titrate the OH radicals to peroxy radicals, even when large amounts of alkene were added to the reactor.

10 mJ/pulse of 320 nm typically produced 50 counts from the first time point after 2000 pulses. The later times points could not be reliably be assigned to RO_2 photolysis.

Geometry 3

The only good information about RO_2 photolysis from geometry 2 is the first point where the photolysis and probe beams were temporally overlapped. For this reason the third geometry (short dashed line, Figure 2) was investigated. This geometry only has one signal point per photolysis pulse as there is no RO_2 photolysis generated between the imaging zone and the pinhole. Therefore the observed signal in this geometry is purely from RO_2 photolyse, hence easy to interpret.

10 mJ/pulse of 320 nm typically generated 70 counts per 1000 photolysis laser pulses, see Figure 3, bottom. Based on the signal of the first time point this geometry yields slightly better signal than geometry 2, but there is one time point of information per UV photolysis pulse.
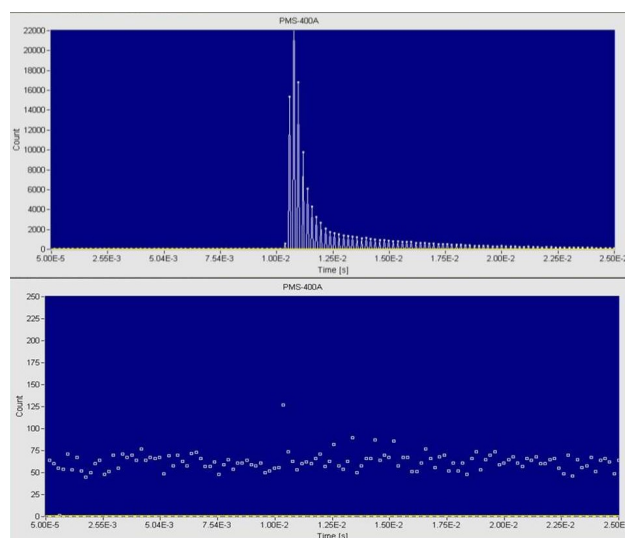

Figure 3. Measured OH signal from the multichannel scaler, MCS. The top trace is from geometry 2 where the UV photolysis laser hits the pinhole and generates a very large and persistent signal after the first time point. The bottom trace is from geometry 3, where there is only signal from the first photolysis time point, at $\sim 10^{-2}$ s on the MCS.

Using geometry 3, the dye laser was scanned between 310 – 330 nm in order to determine the relative cross-section of RO_2 photolysis to produce OH, $\sigma_{RO2,OH}$. The signal decreased with increasing wavelength, which is consistent with the absolute cross-section values obtained in the three laser experimental setup in Figure 1b. The results are shown in Figure 4.
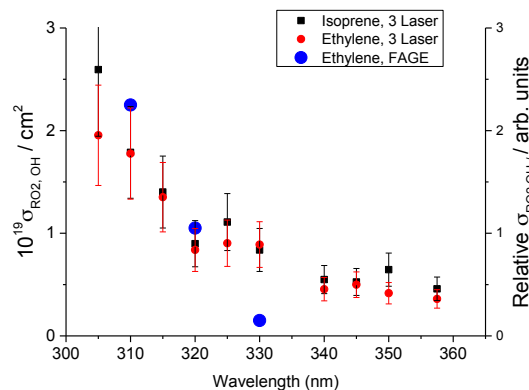

Figure 4. The cross-sections for OH formation from RO_2 (R = isoprene or ethylene) photolysis, $\sigma_{RO2,OH}$ using the flash photolysis experiment in Figure 1b. Relative cross-sections (normalized for dye laser photolysis energies and 1000 pulses) from the low pressure FAGE experiment in Figure 1c show the same trend (blue circles).

The $\sigma_{RO2,OH}$ from the present study are relative as the system is not calibrated. However, the system may be calibrated by assigning the present results to the absolute values from the three laser experiment. The advantage of the present experiments is that it is a quick method to generate the relative $\sigma_{RO2,OH}$ as a function of wavelength. In the reactor reagents may be mixed after the Hg lamp, where the radicals are created. This opens up the possibility of studying a wider range of radicals, e.g. aromatic derived peroxy radials, which are not made cleanly via flash photolysis due to significant reagent photo-dissociation.

Conclusions

A low pressure FAGE cell was used to sample from a reactor where an Hg lamp continuously generated peroxy radicals. The peroxy radicals inside the FAGE cell were photolysed in the near UV with a pulsed dye laser using three geometries, and any OH formed was detected by a second laser. All three geometries suffered from the fact that the 5 kHz FAGE probe laser only measured OH when the 10 Hz UV laser was fired. So the duty cycle of the experiment is effectively 10 Hz. In addition, in geometry 1 only a small fraction of the photolysed molecules reached the imaging zone. Geometry 2 suffered from the huge non-peroxy radical OH signal from UV laser hitting the pinhole, so only the first time point was meaningful. The third geometry essentially only measured peroxy radical photolysis, but it only measured one OH time point per UV pulse, i.e. the duty cycle of this experiment is 10 Hz. Geometry 3 is shown to measure the relative cross-section of RO_2 photolysis to produce OH, $\sigma_{RO2,OH}$, that is consistent with the three laser experiment, Figure 1b. The results from Figure 4 indicate that peroxy radical photolysis in the UV is a minor but not insignificant source of OH in the atmosphere.

Overall, peroxy radical photolysis in a low pressure FAGE cell was demonstrated but the potential advantage of using a high repetition rate OH probe laser was not realized, and in most cases the three laser experiment, Figure 1b, is more straightforward.

References

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