Supplementary Material for PCCP

Reaction of Gas Phase OH with Unsaturated Self-Assembled Monolayers and Relevance to Atmospheric Organic Oxidations

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Supplementary Information

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Description of Reaction Cell: The cell shown in Figure 1 of this paper was developed to study the reactions of gases with self-assembled monolayers and thin films in real time. The cell is divided into two parts: the bottom holder in which the ATR crystal is mounted, and a top rectangular cover through which gases flowed. The bottom consisted of a horizontal attenuated total reflectance (HATR) trough plate (Pike Technologies) in which ~ 3.6 cm^2 of the crystal surface is available for reaction. The plate fits on the HATR base assembly which holds the optics that direct the infrared beam into the crystal and from the crystal to the detector.

The top part of the cell is a custom-designed and machined rectangular cover (7.5 cm × 0.6 cm × 3.3 cm) with a flat base (11.5 cm × 4.5 cm × 0.5 cm) that is attached using screws to the HATR trough plate. The flat base has an oval O - ring groove that provides a seal. The chamber has a volume of 15 cm^3. It has two circular quartz windows (REFLEX Analytical Corporation, 10 mm diameter, 2 mm thickness) on opposite ends of the cell. The top side of the chamber has a groove holding an O-ring where a flat rectangular quartz window (8.5 cm × 2cm × 0.6 cm) is mounted so the crystal can be visually examined and for direct photolysis of the surface film in future studies. The top quartz window is kept in place by another anodized aluminum piece that is screwed on the top of the chamber. There are three gas inlets located along the length of the chamber near the top. Two outlets are located on the opposite side near the bottom of the cover. Gases enter the cell through Teflon tubing mounted onto the Luer lock fittings attached to the inlets that can be easily removed for cleaning.

Light was coupled into the cell using a liquid light fiber optic (Edmund Optics, 5 mm × 6 ft, Model NT53-691) that has high transmittance in the UV region. One end of the fiber optic has a collimating UV transmitting lens (Edmund Optics) threaded to an opening in the sampling compartment of the spectrometer that is centered on the end quartz window of the reaction cell. The other end of the fiber optic is directed towards the photolysis lamp and also has a collimating lens. In order to minimize heating of the fiber optic due to infrared radiation, a 10 cm water filter was placed between the lamp (Spectral Physics, 300 W high pressure Xe, Model 6258 OF) and the fiber optic.

Calculation of OH Concentrations in the Photolysis Beam and at the Surface:

As described in the text, the first order decay of IPN (3.25×10^{17} molecules cm^{-3}) in air was monitored using UV-vis spectroscopy in the static mode. Absorbance spectra were recorded every 5 minutes for approximately 90 minutes. The average first-order rate constant for decay of IPN over three runs was measured to be $(7.0 \pm 0.17) \times 10^{-5}$ s^{-1}. However, IPN decays not only through photolysis but also through secondary reactions, particularly of OH with the IPN ($k = 4.1 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}).

A model of the photolysis of IPN in air was developed that consisted of 111 gas phase reactions for which the differential equations for the kinetics were numerically integrated using Acuchem.[1] The mechanisms and rate constants for the reactions are mostly well-known[2-4] except for the photolysis rate constant of IPN, k_p, which is unique to the experimental system. The photolysis rate constant was extracted by varying the value of k_p to obtain a best fit to the experimentally measured decay of IPN, giving $k_p = (5.0 \pm 0.3) \times 10^{-5}$ s^{-1}. The calculated OH concentrations in the direct path of the light beam varied from $(4.9 - 5.8) \times 10^7$ molecules cm^{-3} over the range of IPN concentrations used, $(0.43 - 17) \times 10^{16}$ molecules cm^{-3}. The OH concentration is relatively insensitive to the IPN concentration. This is because reaction with IPN is a major loss process for OH so that changing IPN changes both production and loss of OH simultaneously.

An unknown parameter needed for the model is the rate constant for loss of OH on the walls of the reaction cell, k_w. The cell was coated with halocarbon wax, which is quite inert towards OH loss. For example, Bertram et al.[5] measured a reaction probability for loss of OH on halocarbon wax of 6×10^{-4}, which for the surface-to-volume of our reaction cell, would correspond to $k_w = 34$ s^{-1}. It is our experience from previous studies using fast-flow discharge tubes coated with halocarbon wax that at relatively high organic concentrations, wall loss of OH can be larger. Thus, in the model, we assumed that in these experiments, 1% of the OH-wall collisions led to loss of OH, $k_w = 6 \times 10^2$ s^{-1}. Using $k_w = 34$ s^{-1} would change the calculated OH concentrations by less than 1% at the largest IPN concentration used and 13% at the smallest IPN concentration. These errors are small compared to those from other sources as discussed below.

As described in the text, the lifetime of OH that is generated within the direct light beam is sufficiently short with respect to reaction with IPN that this does not reach the SAM. It is only the OH that is generated essentially at the crystal surface that is available for reaction with the SAM. Light reaches the crystal surface via internal scattering in the cell, and is much lower in intensity than the direct photolysis beam. Measurements of the integrated light intensity between 300 and 402 nm were made using an Ocean Optics, (Model HR 4000 CG- UV-NIR) spectrometer at positions along the length of the opening in which the crystal was mounted during the experiments, and compared to the light intensity passing directly through the cell. It was found that the intensity along the opening that normally held the crystal was variable along the length. Hence, the opening was divided into 6 regions along the length. Region 1 (r1) constituted 22% of the total area of the crystal, regions 2 - 4 (r1, r2 and r4) were of same area and each constituted 19% of the total area, region 5 (r5) was 17% of the total crystal area and region 6 (r6) was 4% of the area. Multiple measurements of the integrated 300 - 402 nm light intensity were recorded and averaged for each region. The integrated intensities were between about a factor of a hundred and a thousand smaller than that for the direct beam, depending on the region. The IPN photolysis rate constants for each region were then calculated by scaling the value of k_p measured for IPN in the direct photolysis beam:

$$k_{pri} = \frac{I_{ri}}{I_{center}} \times k_p$$

In this calculation, k_p is the photolysis rate constant determined for IPN in the direct photolysis beam, which is $(5.0 \pm 0.3) \times 10^{-5}$ s^{-1}, k_{pri} is the photolysis rate constant for IPN in region i ($1 \leq i \leq 6$) and I_{ri} and I_{center} are the integrated light intensities at region i and and for the beam that has passed directly through the center of the cell. The OH concentration for each region was then calculated based on the respective photolysis rate constants and the 111-reaction model of IPN photolysis in air. The average OH concentration to which the SAM was exposed was then calculated as a weighted average of these concentrations, where the weighting is based on the relative areas of the different regions:

$$OH_{average} = 0.22\ OH_{r1} + 0.19(OH_{r2} + OH_{r3} + OH_{r4}) + 0.17\ OH_{r5} + 0.04 OH_{r6}$$

This value of the OH concentration was then used to determine the reaction probability as described in the text. As noted above, the steady-state OH concentration is given approximately by k_p/k_1 and hence is independent of the initial IPN concentration. The average value of [OH] used to determine γ in all runs was 2.1×10^5 OH cm^{-3}. The uncertainty in this concentration is determined primarily by the error in measuring k_p at the crystal surface, which is itself determined by the measurement of the average light intensities at the surface. Applying standard error analyses[6] to the surface light intensity measurements suggests that the uncertainty in the OH concentration is a factor of 1.6.

References

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