Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Influence of humidity and iron (III) on photodegradation of atmospheric secondary organic aerosol particles

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1. PTR normalization for different RH

The relative abundance of $H_3{}^{18}O^+$ and $H_3O^+(H_2O)$ in the PTR-ToF-MS ion source changes as a function of RH, resulting in an RH-dependent sensitivity for the detection of certain VOCs with low proton affinities, such as benzene,[1] monoterpenes[2] and formaldehyde.[3] The detected organics react at different rates with H_3O^+ and with $H_3O^+(H_2O)$, making their ionization efficiency RH-dependent. We define X_R as the ratio between the reaction rate of an organic molecule with $H_3O^+(H_2O)$ and H_3O^+. X_R is around 0.48 and 0.58 for acetaldehyde and acetone and in general is 0.5 for organics which do not contain aromatic rings.[4, 5] We consider X_R to be 0.5 for formic acid and acetic acid. Because we are only interested in relative concentrations, we normalized the signal observed at different RH to what it would have been at 0% RH:

$$S'_{VOC}(corrected) = S_{VOC}(measured\ at\ RH) \cdot \frac{\left(S_{H_3O^+} + X_R S_{H_3O^+(H_2O)}\right)_{0\%\ RH}}{\left(S_{H_3O^+} + X_R S_{H_3O^+(H_2O)}\right)_{RH}} \qquad \text{(S1)}$$

Table S1. Measured signal of $H_3{}^{18}O^+$, derived signal $H_3{}^{16}O^+$ (obtained from the signal of $H_3{}^{18}O^+$ by scaling) and signal of the $H_3O^+(H_2O)$ measured at different RH.

RH	Signal of $H_3{}^{18}O^+$ (counts/s)	Inferred signal of $H_3{}^{16}O^+$ (counts/s)	Signal of $H_3O^+(H_2O)$ (counts/s)
0%	4,100	2,050,000	80,000
10%	4,500	2,250,000	120,000
25%	4,700	2,350,000	270,000
40%	4,700	2,350,000	350,000
55%	4,500	2,250,000	150,000
70%	4,500	2,250,000	200,000

We checked for the presence of ionic clusters between protonated organic molecules and water. For formic acid, at 25% RH and 40% RH for the signal due to the $[M+H+H_2O]^+$ cluster was 2% and 3%, respectively, of the protonated ion $[M+H]^+$. For the rest of the ions, the cluster contribution was below 1%. Therefore, we do not take clustering into account because it does not affect the signal significantly.

2. Kinetic Multi-Layer Modeling

We developed a kinetic multi-layer model of release of volatile compounds from films that explicitly evaluate diffusion and release of volatile compounds from the films to the gas phase, resolving concentration gradients and diffusion throughout the film and release into the gas phase.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{(S2)}$$

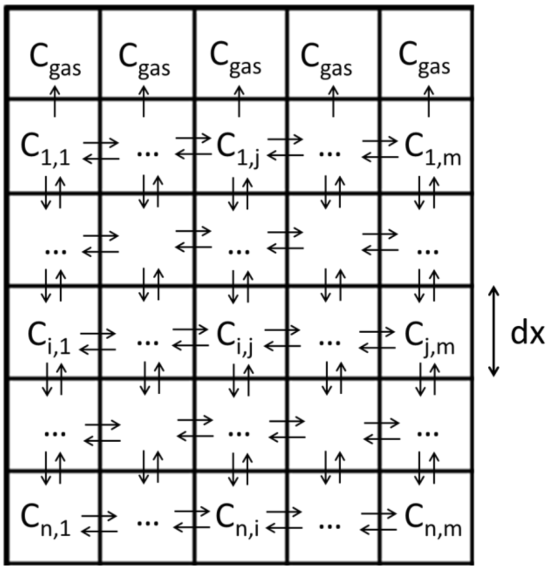

Figure S1. Model compartments and layers in which the film is divided. The arrows represent the diffusion that occur between different compartments. The dimension of the compartments is represented by *dx*.

The bulk of the film is divided in n layers (numbered 1,2,3,…,n) and m columns (numbered 1,2,3,…,m) as shown in Fig. S1 leading to a mesh of compartments. Each of these can compartments exchange mass with the four adjacent ones. For our system we defined the concentration in the gas phase as 0, leading just to release but not uptake. Another boundary condition was to make equal the concentration in the last layer in the three edges to the concentration in the second last layer to be able to apply Eq. S2 in every compartment:

C(n,j)=C(n-1,j) for j=1,2,…m (S3)

C(i,1)=C(i,2) for i = 1,2,...n (S4)

C(i,m-1)=C(i,m) for i = 1,2,...n (S5)

Following the diffusion equation Eq. S2, and assuming an initial profile, the mass transport is evaluated in the film by applying Eq. S6 to every cell for a certain number of time intervals which length is defined by *dt*:

C(i,j,t)= C(i,j,t-1)+ dt * D * C(i+1,j,t-1)+ C(i,j+1,t-1) - 4* C(i,j,t-1) + C(i-1,j,t-1) + C(i,j-1,t-1)/dx /dx) (S6)

We defined a system with n=30 layers and m=50 columns which led to a mesh of 150 compartments. The time interval used for the predictions was 0.1 s extending the predictions up to 200 seconds. We optimized the values of the diffusion coefficients (D) at different RH by fitting the release predicted by the model to the observed decay of acetaldehyde after switching off lights as shown in the main text. We tested the sensitivity of two initial concentration profiles on the diffusion coefficient parameter to reproduce our data: i) uniform initial concentration profile is flat throughout the film and ii) linear initial concentration profile where its maximum concentration is in the bottom of the film and zero at the surface.

References

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