Interactive comment on “Influence of relative humidity and temperature on the production of pinonaldehyde and OH radicals from the ozonolysis of α-pinene” by R. Tillmann et al.

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Received and published: 11 February 2010

In my opinion, the authors are labeling the direct uptake of water too quickly as a negligible process. As discussed in section 3.2, an increase in mass fraction of about 0.03 at 253K for the wet vs. the dry case (Fig. 4) is obtained (one assumes that the particle is liquid at this temperature). However, the mole fraction increase is much larger. Assuming that the mean molar mass $\text{MW}_{\text{om}} = 180$ g/mol assumed by the authors, is representative for the dry system, i.e. $\text{MW}_{\text{om}} = M_{\text{org}}$, with $M_{\text{org}}$ the mean molar mass of the organic (without water) fraction, one directly obtains

$$X_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{org}} + n_{\text{H}_2\text{O}}}$$

$$= \frac{m_{\text{H}_2\text{O}}}{m_{\text{org}}M_{\text{H}_2\text{O}}/\text{MW}_{\text{om}} + m_{\text{H}_2\text{O}}}$$

$$= \frac{f_{\text{m,H}_2\text{O}}M_{\text{H}_2\text{O}}/\text{MW}_{\text{om}} + f_{\text{m,H}_2\text{O}}}{(1 - f_{\text{m,H}_2\text{O}})M_{\text{H}_2\text{O}}/\text{MW}_{\text{om}} + f_{\text{m,H}_2\text{O}}}$$

$$\approx 0.24$$

with $f_{\text{m,H}_2\text{O}}$ the mass fraction of water. If on the other hand the $\text{MW}_{\text{om}} = 180$ g/mol is representative of the wet case, for the total (organics+water) system, then

$$X_{\text{H}_2\text{O}} = \frac{f_{\text{m,H}_2\text{O}}\text{MW}_{\text{om}}}{M_{\text{H}_2\text{O}}} \approx 0.3$$

$$M_{\text{org}} = \frac{1 - f_{\text{m,H}_2\text{O}}}{\text{MW}_{\text{om}} - f_{\text{m,H}_2\text{O}}} \approx 249.4$$

In either case the mole fraction of H$_2$O is quite significant. Rewriting Pankow’s equation for molar concentrations instead of mass concentrations (see Compernolle et al. (2009); Barley et al. (2009)), one obtains:

$$\frac{c_{p,i}}{c_{g,i}} = \frac{\kappa_{p,i}c_{\text{tot}}}{\kappa_{g,i}c_{\text{tot}}} = \frac{RT}{\gamma_i}c_{\text{tot}}$$

$$= \kappa_{p,i} (c_{\text{org}} + c_w)$$

with $c_{\text{tot}}$ the amount of aerosol (including water if it is present) in mole concentration and $c_{\text{org}}, c_w$ the concentrations of organics and water respectively. $c_{\text{tot}}$ will be increased significantly in the wet case due to the uptake of water. This will lead to increased partitioning (higher $c_{p,i}$, and this in turn will increase both $c_{\text{org}}$ and $c_w$. In this way, the uptake of water results - indirectly - also in a significant mass increase. Fig. 3 in Compernolle et al. (2009) illustrates this phenomenon. The modelled mass yield increases with RH, but - certainly at low and medium RH - this increase is mainly due to the mass increase of organic part, not due to the mass increase of the water
part. But as explained above, this increase is indirectly caused by the significant molar increase of water. The amount of increase will depend on the concentrations of the products and their vapor pressures.

In conclusion, the water uptake could explain to some extent the higher mass yields observed by the authors in the humid case, so the authors should pay attention to this.

A related issue is the value of $MW_{om}$, which will be quite different (as illustrated above) for dry and wet cases, but seems to be fixed to one value (180 g/mol) by the authors.

We certainly do not suggest that RH has no important effect on the reaction paths. One way to distinguish between water-uptake-induced SOA increase (1) and SOA yield due to changes in reaction paths (2) is to increase the RH at a moment when the $\alpha$-pinene has already reacted, such that (2) will not occur.

References


Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3129, 2010.