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Comment

Interactive comment on “HCOOH measurements from space: TES retrieval algorithm and observed global distribution” by K. E. Cady-Pereira et al.

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Comment by J.-F. Müller and J. Peeters

Although not essential to the main purpose of this article, which is the presentation of a new dataset of formic acid abundances retrieved from the TES instrument, we want to comment on a specific chemical process included in the model simulations presented in Section 4 of this paper: the photo-induced tautomerization of acetaldehyde to vinyl alcohol (VA) followed by oxidation of VA by OH to formic acid. Two recent laboratory studies (Andrews et al., 2012; Clubb et al., 2012) have proposed that this process might be a large source of formic acid in the atmosphere, possibly explaining (part of) the “missing” source of formic acid inferred from atmospheric observations (Paulot

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et al., 2011; Stavrou et al., 2012). Based on the laboratory-derived tautomerization quantum yield (15–21% or up to a factor of 1.5 larger than the photodissociation quantum yield), and using a recent state-of-the-art model estimate of the acetaldehyde photolysis sink (Millet et al., 2010), it can be roughly estimated that acetaldehyde photo-tautomerization might generate as much as 23–33 Tg vinyl alcohol annually. If entirely converted to formic acid, this would represent a source of ca. 25–35 Tg HCOOH per year, which is indeed substantial.

However, the reaction of VA with OH has to compete with the keto-enol tautomerization of VA to its much more stable form, acetaldehyde. In absence of any catalyst, keto-enol tautomerization is negligible (Yamada et al., 1999). But, catalyzed by formic acid, present in the continental boundary layer at concentrations of the order of 1 ppbv (Stavrou et al., 2012), it is likely by far the dominant sink of VA: with a rate of $1.3 \cdot 10^{-14} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ (da Silva et al., 2010), the reaction of VA with formic acid should proceed at a rate of typically $2 \cdot 10^{-5} \text{ s}^{-1}$ i. e. an order of magnitude faster than reaction with OH, using $[\text{OH}] \sim 3 \cdot 10^6 \text{ molec. cm}^{-3}$ and a reaction rate of $6 \cdot 10^{-12} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ (Archibald et al., 2007). Tautomerization to acetaldehyde might be even faster, due to the presence of other catalysts such as aerosol surfaces. The role of heterogeneous catalysis is suggested by the observed very fast conversion of VA to acetaldehyde in laboratory conditions (Tadic et al., 2012), likely due to catalysis on the chamber walls.

In conclusion, the photo-induced tautomerization of acetaldehyde is likely, at most, a minor atmospheric source of formic acid, crudely estimated here at ~ 3 Tg per year globally, possibly less.

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