On the formation of formic acid from formaldehyde processing in liquid clouds

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Abstract

It was recently proposed (Franco et al., Nature 2021) that methanediol (MD, HOCH2OH) formed by hydration of formaldehyde in liquid cloud droplets is outgassed to a larger extent than previously estimated, and reacts in the gas phase with the hydroxyl radical (OH), leading to formic acid (HCOOH). Whereas the resulting global production of formic acid is greatly dependent on poorly constrained parameters, such as the Henry's law constant (HLC) of methanediol and the rate constant of its reaction with OH, Franco et al. suggest, based on global model calculations and on newly conducted chamber experiments (for the rate constant) and on statistical prediction methods (for the HLC), that this mechanism explains the large "missing source" of HCOOH in the atmosphere (e.g. Stavrakou et al. 2012). If true, this finding would be of tremendous importance for our understanding of the biogeochemical cycling of oxygenated organic compounds. For this reason, it is of utmost importance to double check the validity of thehypotheses and parameterizations behind this assessment. Here we examine two critical aspects of this determination: the HLC (taken equal to either 10ˆ4 or 10ˆ6 M atmˆ-1 in model simulations by Franco et al.) and the rate of the MD+OH reaction (taken equal to 7.5 × 10ˆ12 cmˆ3 sˆ-1). The representation of chemical processing in liquid clouds in global models is also briefly discussed. Plausible ranges for those parameters are proposed , and causes of uncertainty are discussed . The potential consequences for the resulting production of formic acid are briefly explored.

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Context

It was recently proposed (Franco et al., Nature 2021) that **methanediol (MD, $HOCH_2OH$) formed by hydration of formaldehyde in liquid cloud droplets** is outgassed to a larger extent than previously estimated, and **reacts in the gas phase with the hydroxyl radical (OH), leading to formic acid (HCOOH).** Whereas the resulting global production of formic acid is greatly dependent on poorly-constrained parameters, such as the Henry's law constant (HLC) of methanediol and the rate constant of its reaction with OH, Franco et al. suggest, based on global model calculations and on newly conducted chamber experiments (for the rate constant) and on statistical prediction methods (for the HLC), that **this mechanism explains the large "missing source" of HCOOH in the atmosphere** (e.g. Stavrakou et al. 2012). If true, this finding would be of tremendous importance for our understanding of the biogeochemical cycling of oxygenated organic compounds. For this reason, it is of utmost importance to double-check the validity of the hypotheses and parameterizations behind this assessment.

Here we examine two critical aspects of this determination: **the HLC** (taken equal to either 10^4 or 10^6 M atm^{-1} in model simulations by Franco et al.) and **the rate of the MD+OH reaction** (taken equal to 7.5×10^{-12} cm^3 s^{-1}). The representation of chemical processing in liquid clouds in global models is also briefly discussed. Plausible ranges for those parameters are proposed, and causes of uncertainty are discussed. The potential consequences for the resulting production of formic acid are briefly explored.

Henry's Law constant of MD

- There is no direct measurement for the HLC of methanediol (H_{MD})
- The HLC of C_2-C_5 alkanediols is of the order of 5×10^5 M atm^{-1} at 298 K (Sander 2015, Burkholder et al. 2020, Compernolle and Müller 2014)
- The statistical method referred to by Franco et al. for H_{MD} (bond method of HENRYWINv3.10) underestimates the HLC of ethanediol by a factor 80
- Mansfield (2020) estimated H_{MD} to ~4×10^5 M atm^{-1} at 300 K, based on the known intrinsic HLC of HCHO (H_{HCHO}) and on the equilibrium constants (diol/aldehyde) in the gas phase (K_g) and in the aqueous phase (K_w): $H_{MD} = H_{HCHO} \times (K_w/K_g)$
- Using Mansfield's result and the gas dissolution enthalpy for ethanediol from Compernolle and Müller, we derive $H_{MD} = 4\times10^5 \exp[8800(1/T-1/300)]$ M atm^{-1}
- At 280 K, the most relevant temperature for liquid clouds, the estimated HLC is therefore **3×10^6 M atm^{-1}**, well above the range considered by Franco et al. (10^4 – 10^6 M atm^{-1})
- Below freezing, in the upper part of liquid clouds, ice impurities were seen to decrease the HLC of organics (Sieg et al. 2009). Nevertheless, based on the median HLC reductions between +5°C and -25°C derived by Sieg et al., we expect the H_{MD} to remain above, or close to, 10^6 M atm^{-1} in this temperature range

The rate of gas-phase reaction of methanediol (MD) with OH

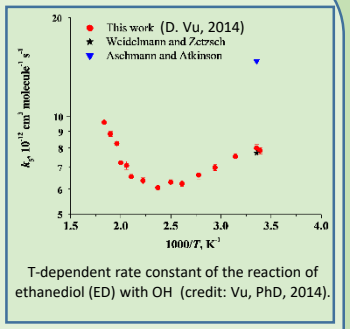
In absence of prior measurement for the rate of gas-phase MD+OH reaction (k), Franco et al. present 3 separate determinations (here at 298K):

1) k_{theo}**= 0.94×10^{-12} cm^3 s^{-1}** based on detailed theoretical calculations (geometries: M06-2X; energies: CCSD(T)/CBS(DTQ))
2) k_{fit}**= 7.5×10^{-12}** (range: (1-10) $\times10^{-12}$) **cm^3 s^{-1}**, based on MD temporal behavior in smog chamber (SAPHIR) experiments in which OH and other compounds were also measured. In the adopted setup, [OH] was high in Stage 2 and negligible in Stage 3, allowing a tentative separation of wall losses from gas-phase chemical loss.
3) k_{reac}**= $20\pm13\times10^{-12}$ cm^3 s^{-1}** based on OH reactivity experiments, assuming that the difference between the measured total OH-reactivity and the sum of individual contributions from measured species is due to reaction with MD.

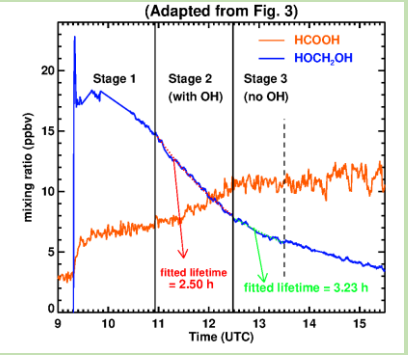
- k_{reac} **is** likely **too high** due to unmeasured species reacting with OH. MD and HCHO were injected as liquid formalin, which can polymerize to poly-(oxymethylene)glycols $HO(CH_2O)_nH$ (Kumar & Francisco 2015), possibly generating numerous compounds. This possibly explains the presence of (otherwise unexplained) CH_3CHO in the system (Fig S2-S3).
- **Wall-related desorption and losses make the derivation of k_{fit} very uncertain** as they cannot be expected to be constant between experiments and even during each experiment.
- Nevertheless, using data from Fig.3 of Franco et al. (see Figure below), we infer a MD chemical lifetime of 1/(1/2.5 – 1/3.23) = 11.1 h, hence ***k*= 3.6×10^{-12} cm^3 s^{-1}** (with [OH]=7×10^{-12} cm^{-3}). Similarly using data from Fig. S3, a value ***k*= 4.1×10^{-12} cm^3 s^{-1}** is derived (not shown)
- Those values, while about **twice lower than** the value **used in model runs by Franco et al.**, are affected **by wall catalysis** and might be overestimations of the relevant gas-phase *k*

What can we learn from 1,2-ethanediol (ED) reaction with OH ?

- Weidelmann & Zetzsch (1982) and Vu (2014) both performed absolute rate measurements for the ED+OH reaction. The reported values are very consistent at 298 K (8.0 and 7.7×10^{-12} cm^3 s^{-1})
- Aschmann & Atkinson (1998) reported a higher value (14.7×10^{-12}) using a relative rate measurement method. However, in the same publication Aschmann & Atkinson reported rate constant measurements for 4 other alcohols that were all about twice greater than previous absolute measurements. The technique involved absorption and desorption of the samples, which can generate large errors.
- MD has **twice less abstractable H's** than ED. Moreover, those H atoms are **less easily abstractable:**
  - ✓ The calculated C-H bond strength in MD (Franco et al.) is ca. 2 kcal mol^{-1} higher than that for a -CH_2OH group as in CH_3-CH_2OH.
  - ✓ Both MD+OH and ED+OH proceed through a pre-reaction complex with the °OH radical H-bonded to an O(H)- group. With ED, H-abstraction from the other carbon can occur through a 6-membered cyclic transition state (TS). For MD, however, only a 5-membered TS is possible. Its much higher ring strain (by several kcal/mol) imply that the MD+OH rate should be **much lower** than half the ED+OH rate.
- Therefore ***k* << 4×10^{-12} cm^3 s^{-1}** , consistent with the theoretical determination of the rate reported by Franco et al. (k_{theo}=0.94×10^{-12} cm^3 s^{-1} at 298 K). Its estimated uncertainty (factor of 3) is probably too high.



T-dependent rate constant of the reaction of ethanediol (ED) with OH (credit: Vu, PhD, 2014).



Measured MD and HCOOH in a SAPHIR experiment and exponential regressions of MD decay in Stage 2 (red) and 3 (green) (adapted from Franco et al.). The fitted lifetimes are also given.

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Conclusions & recommendations

- **The Henry's law constant of methanediol (H_{MD}) is likely >10^6 M atm^{-1} in relevant conditions**
- The temperature-dependence (e.g. the expression $4\times10^5 \exp(8800(1/T-1/300))$ M atm^{-1} derived in this work) should be included in model simulations
- Including a correction for the effect of ice clusters is recommended, not just for MD but for all organics including HCHO. This will *decrease* the overall importance of the cloud-mediated HCOOH source.
- **The theoretical determination of the MD+OH rate (0.94×10^{-12} cm^3 s^{-1} at 298 K) is the best available estimate and is consistent with previous laboratory results for ED+OH.**
- Careful laboratory determinations of the MD+OH rate constant are clearly needed to confirm the above conclusion
- A major uncertainty lies in the model representation of multiphase processes involving clouds. When an MD molecule is expelled from a droplet, it generally remains surrounded by cloud droplets and will mostly return to the aqueous phase. Especially in stratified clouds (e.g. Stratus), an MD molecule would reside in cloud droplets for far too long, such that aqueous chemical processing is the dominant sink