

[Interactive
Comment](#)

Interactive comment on “Complex chemical composition of colored surface films formed from reactions of propanal in sulfuric acid at upper troposphere/lower stratosphere aerosol acidities” by A. L. Van Wyngarden et al.

Anonymous Referee #3

Received and published: 31 December 2014

This manuscript reports on the chemical characterization of colored surface films formed from the reaction of propanal and propanal mixed with glyoxal and/or methylglyoxal with sulfuric acid under acidity conditions typical of upper troposphere/lower stratosphere (UT/LS) aerosols. The experimental approach relies on a combination of ATR-FTIR, ¹H NMR, and UV-VIS spectroscopies to identify potentially surface-active reaction products and the chemical pathways leading to their formation. As mentioned in the manuscript, there has been recently some interesting research devoted at characterizing reaction products from simple aldehydes (and their mixtures) in sulfuric acid

C10617

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



and acidic aqueous salt solutions in the context of tropospheric aerosol chemistry. However, the present work goes further by specifically focusing on the chemical characterization of "interfacial" species. More importantly, it adds a step in complexity by addressing the possibility of cross-reactions in more atmospherically-relevant mixtures. That said, some unknowns still remain to be elucidated, e.g., the kinetics of these reactions, the interplay of different aldehydes in mixtures, as well as the identification of the minor species responsible for the strong visible absorption. The elucidation of interfacial reaction products and their underlying reaction mechanisms as proposed in this work is atmospherically relevant as they directly influence the chemical and optical properties of UT/LS aerosols. Overall, the manuscript is well written and well documented. Only a few minor comments/questions/suggestions (see below) would need to be clarified prior to publication.

P28579, L19-L27: There are many quantitative trends inferred by the authors about the film formation rates, e.g. films form faster at higher acidity, mixed glyoxal films forming faster than mixed methylglyoxal ones, etc. Even though the authors recognize the variability between replicates, would it be possible for them to give at least some estimate or range on the timescale (min, hr, etc.) of these rates? It is not clear to me what "slower" or "faster" means here.

P28581, L1: ATR-FTIR spectra were taken on 7 day old surface films. I'm wondering if the authors also checked the same spectra on older films? In other words, is there a detectable aging effect on their films and on what timescale? Days, months or more? This would be interesting to know as they show the importance of such an effect in their UV-VIS spectra in Fig. 7 (although at a lower organics concentration)? Following the aging of these films could give some information about the time evolution of some interfacial species. It would be interesting to know if some transient species also show up.

P28583, L13 and Fig. 2 caption: The authors mentioned that the ATR-FTIR spectrum of 2,4,6-triethyl-1,3,5-trioxane was not shown as the product is not commercially avail-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

able (although they do come up with a close chemical analogue, TCI). This statement is perhaps too strong and may not be entirely true. In fact, this specialized organic product is commercialized and can be obtained from a few suppliers (e.g., BOC Sciences, New York, USA; Angene International Ltd, Honk-Kong, China).

P28587, L17-22: These two observations are interesting. Was there any experiment done to verify that glyoxal participation in film-forming reactions could indeed be inhibited by methylglyoxal? I would suggest looking at the FTIR spectra from mixed solutions with different glyoxal/methylglyoxal ratios (e.g., 1:5, 1:3, 1:2, 2:1, 3:1, 5:1). Also, can the authors provide a possible mechanism (in one or two sentences) that could explain this inhibition by methylglyoxal?

P28603, Fig. 2: I think the authors and readers would benefit by having the "major" peaks (or at least the peaks that the authors want us to look at) identified (e.g., wavenumber, type of vibrational mode) directly on the spectra. This would allow for a quick read of the figure. In comparison, the ^1H NMR spectra of Fig. 3 arrangement are quite easy to read and understand. Another possibility would be to have a small table with wavenumbers, assignments and tentative products identification somewhere in the text.

P2(Supplement), Fig. S1: The image of the left panel is too blurry and would need to be replaced.

P28575, L1&4: Replace "surface active" by "surface-active".

P28575, L8: Replace "by letter" by "by a letter".

P28576, L6: Replace "and or" by "and/or".

P28580, L11: Replace "(our standard) respectively" by "(our standard), respectively".

P28582, L14: Replace "the 2 most" by "the two most".

P28597, L12: Replace "cross reactions" by "cross-reactions".

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

P28607, Fig. 6: Remove box around legend to be consistent with other figures.

P28608, Fig. 7: Format the plot axis titles (no boldface) to be consistent with other figures.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 28571, 2014.

ACPD

14, C10617–C10620,
2014

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

C10620

