

We sincerely thank all three referees for their helpful, insightful and thorough reviews that have helped us to significantly improve our manuscript. Below, each reviewer comment is listed followed by our responses in blue and changes to the manuscript in *blue italics*.

### **Response to Anonymous Referee #3:**

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.

Please see our response to referee #2 who requested similar information in reference to the same ACPD line number (P28579, L19).

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.

NMR and ATR-FTIR spectra of older and younger films (1, 4, 68 and 134 days old) all show the same major species as the 7 day old films with some detectable trends in relative peak ratios with age. These results are related to some additional results requested by Referee #2 and are therefore described together in the text below that has been added to the manuscript as a new section (3.3):

#### ***“3.3 Effects of light exposure, temperature, propanal concentration and film age***

*The preceding detailed chemical analyses were presented for the base case of a film formed on a 7 day old solution of 0.30 M propanal in 48 wt % sulfuric acid, stored at room temperature under fluorescent room light. Very similar NMR spectra were obtained from films formed on solutions that were stored under different conditions (dark and/or 0°C), that were younger (1 and 4 days) and older (68 and 134 days), or that were formed at lower propanal concentration (0.030 M); and these spectra confirm the presence of the same major chemical species. Spectra of films formed in the dark are not detectably different than those formed in the light, but films formed at different ages, at 0°C, or at lower propanal concentration display the following significant differences in relative peak areas between chemical species when compared to the base case.*

*There were two detectable trends in NMR peak area ratios with film age. First, the trioxane (4.75 ppm) peak area decreased with age relative to all other species that produced peaks separated well enough for integration [2-methyl-2-pentenal (9.39 ppm), trimethylbenzene (6.79 ppm) and propanal (9.79 ppm)]; furthermore, the oldest samples (68 and 134 days) lacked any*

*detectable trioxane. Trioxane peaks also decreased relative to the peaks in the ATR-FTIR spectra assigned to long-chain polymers. Therefore, since trioxane decreases with time relative to all other major film species and the films grow thicker with time, it is possible that trioxane is initially formed rapidly, followed by slower formation of all other film species. Second, the trimethylbenzene (6.79 ppm) to 2-methyl-2-pentenal (9.39 ppm) peak area ratio increased with age (by a factor of 2 to 3 going from 1-7 day old samples to 68 and 134 day old samples). Since 2-methyl-2-pentenal is a precursor for trimethylbenzene formation, this result suggests that trimethylbenzene formation continues beyond one week.*

*Although solutions stored at the lowest temperature of -19°C did not produce sufficient quantities of film for analysis, the NMR spectrum of a 73 day old film formed at 0°C showed higher relative levels of trioxane and lower relative levels of trimethylbenzene than those formed at room temperature. This result is consistent with reactions that proceed more slowly at lower temperature, according to the previously noted trends with age.*

*Finally, solutions with lower propanal concentration (0.030 M vs. 0.30 M) did not produce a sufficient quantity of film for reliable removal and spectral analysis without contamination by the underlying sulfuric acid solution. However, one weak NMR spectrum of a 16 day old sample was obtained that allows positive detection of trimethylbenzene and 2-methyl-2-pentenal and that indicates likely presence of long-chain polymers due to multiple overlapping peaks similar to those previously assigned to protons on the polymer ethyl chains (1.0-1.7 ppm and ~0.94ppm). Trioxane could not be detected above the noise; but we note that low trioxane content could be due to the older film age since the trimethylbenzene to 2-methyl-2-pentenal ratio is high and therefore also consistent with older films formed on 0.30 M propanal solutions.”*

Additionally, the text shown in blue below was added as shown to the text at P28580, L20-25.

*“The detailed chemical analysis in these sections is presented for surface films formed on 0.30 M propanal/48wt % H<sub>2</sub>SO<sub>4</sub> as a starting point, since surface films were only formed on solutions containing propanal and since propanal formed films fastest at 48 wt % H<sub>2</sub>SO<sub>4</sub>. These films were stored at room temperature under constant fluorescent light and were sampled and analyzed 7 days after mixing the solutions. Sections 3.3-3.5 subsequently address the impact of varying the temperature, illumination, organic concentration, film age, acidity and organic mixture from this base case.”*

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 available (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).

At the time of writing we had contacted many potential suppliers of 2,4,6-triethyl-1,3,5-trioxane. Although a few suppliers listed it on their websites (including the suppliers mentioned by the referee), none had any in stock nor any plans to produce more, although one supplier (AKos GmbH) did offer expensive custom synthesis as an option. Since we completely agree with the referee that it would be more illustrative to include its ATR-FTIR spectrum in Figure 2, we proceeded with custom synthesis and as a result are pleased to include its spectrum in Figure 2

(replacing the spectrum of the close analog). Along with this change to the figure, the following changes to the text (shown in blue below) are also made:

P28583, L2-16:

*Of these potential products, the cyclotrimer is most easily confirmed since it is readily identified by comparison of the FTIR and NMR spectra of the film to ~~the reference~~ spectra (SDBS) of 2,4,6-triethyl-1,3,5-trioxane as indicated by the peaks assigned to the trioxane (T) in Figs. 2 and 3. Specifically, the <sup>1</sup>H NMR spectrum of the film contains all three of the peaks in the reference spectrum (SDBS): a triplet at 4.78 ppm, a complex multiplet at 1.67 ppm and a triplet at 0.94 ppm (although the broad peak group at 0.94 ppm can only be partially due to the trioxane due to its strong intensity relative to the other trioxane peaks). Similarly, as shown by assignments in Fig. 2, at least 13 peaks in the FTIR spectrum of the film correspond within 2 cm<sup>-1</sup> to peaks in the ~~reference~~ spectrum of ~~a neat liquid film of~~ 2,4,6-triethyl-1,3,5-trioxane (including all 6 of the strongest ~~reference~~ peaks between 1500-900 cm<sup>-1</sup>). ~~(This trioxane is not commercially available, so in order to also provide a general idea of relative peak intensities expected in the ATR-FTIR spectrum of the trioxane, the spectrum of a trioxane that differs only by replacing one ethyl group with a methyl group (2,4-diethyl-6-methyl-1,3,5-trioxane) is also shown in Fig. 2.)~~*

Fig. 2 caption:

Original text:

*“Spectra of standards for propanal, 2-methyl-2-pentenal and 1,3,5-trimethylbenzene are scaled to indicate their maximum possible contribution to the film spectrum. The spectrum of the trioxane formed by propanal, 2,4,6-triethyl-1,3,5-trioxane, is not shown since it is not commercially available; instead the peak positions from a reference spectrum (SDBS) are indicated with the abbreviation T. Additionally, the spectrum of a similar trioxane, 2,4-diethyl-6-methyl-1,3,5-trioxane, is shown in order to provide an idea of expected relative peak intensities.”*

The preceding original text is replaced by:

*“Spectra of standards for propanal, 2-methyl-2-pentenal, 1,3,5-trimethylbenzene and 2,4,6-triethyl-1,3,5-trioxane are scaled to indicate their maximum possible contribution to the film spectrum. The positions of the major trioxane peaks are indicated with the abbreviation T to illustrate their presence in the spectrum of the film”.*

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?

FTIR spectra were examined from films formed on mixed propanal/glyoxal/methylglyoxal solutions with lower methylglyoxal concentrations, corresponding to glyoxal/methylglyoxal ratios of 2:1, 3:1, 10:1 and 100:1. The spectra remained similar to spectra of the propanal/methylglyoxal mixtures for all but the lowest methylglyoxal concentration which matched the propanal/glyoxal spectra as would be expected. The text shown in blue below was added to report the result that the “inhibition” effect was observed in the FTIR spectra even at

10x lower methylglyoxal concentration and to suggest plausible mechanisms, although we note that, due to the complexity of this system, much further work would likely be required to explain these results.

*“Finally, it is intriguing that 1) the spectrum of the film formed on the propanal/glyoxal/methylglyoxal mixture is quite similar to that for the propanal/methylglyoxal mixture, differing only in relative peak ratios (a result that remained true even when the methylglyoxal concentration was reduced by up to a factor of 10, but not by a factor of 100) and 2) that the rate of film formation was decreased from the rate for the propanal/glyoxal mixture. This could indicate that glyoxal is somehow inhibited from participating in film-forming reactions by the presence of methylglyoxal. The mechanism for such inhibition is unclear, but plausible explanations include cross reactions of glyoxal with methylglyoxal that are faster than those with propanal, but that do not result in products that partition to the film and/or dimerization reactions of propanal with methylglyoxal that are faster than those with glyoxal, but that subsequently require more time to form polymers that are large enough to partition into the film.*

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 <sup>1</sup>H 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.

We have added wavenumber labels and assignments of the most important peaks to Figure 2 and agree that this improves the figure.

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

We agree and have replaced the photo with two better ones.

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

We have revised as recommended.

P28575, L8: Replace “by letter” by “by a letter”.

We have revised as recommended.

P28576, L6: Replace “and or” by “and/or”.

We have revised as recommended.

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

We have revised as recommended.

P28582, L14: Replace “the 2 most” by “the two most”.

We have revised as recommended.

P28597, L12: Replace “cross reactions” by “cross-reactions”.  
[We have revised as recommended. \(This typo was actually on P28587\).](#)

P28607, Fig. 6: Remove box around legend to be consistent with other figures.  
[We have revised as recommended.](#)

P28608, Fig. 7: Format the plot axis titles (no boldface) to be consistent with other figures.  
[We have revised as recommended.](#)