

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 #2:

P28577, L8-11: My reading of this sentence is that each organic is present in a mixture at 0.030 M ie. a mixture of propanal in sulfuric acid will contain 0.030 M of propanal, and a mixture of propanal and glyoxal in sulfuric acid will contain 0.030 M propanal and 0.030 M glyoxal. If this is the case, then the total concentration of organic in a solution will depend on whether 1, 2 or all 3 aldehyde species are in the mixture. I am not confident that the impact of different chemical species on the rate of film formation can be directly compared if the total organic loading is being altered as well as the composition of the aldehyde fraction.

The referee is correct in the interpretation that samples were prepared with 0.030 M of each organic present so that samples with a larger number of organic species also have a higher total organic concentration. This comment raises an important point that our comparison of film formation rates among the various organic mixtures is not really analogous to comparison of chemical reaction rate constants of self- vs. cross-reactions. Instead, the experiments were designed this way as a simple method of detecting whether or not the presence of glyoxal and/or methylglyoxal had *any* impact on the ability of propanal to form films. (Since glyoxal and/or methylglyoxal did not form films in the absence of propanal they could potentially have been mere spectators or participated in cross-reactions that were more or less likely to result in products that form surface films.) If we had altered the propanal concentrations to maintain constant total organic, we would not be able to exclude the possibility that altered film formation rates were due simply to different starting concentrations of propanal. However, this means that our observed increases in film formation rates with addition of glyoxal indicate that cross-reactions occur, but not necessarily that cross-reaction rates are larger than self-reaction rates. We have added text to clarify this in two places. First, the following was added immediately after the sentence referenced by the referee:

“Since initial experiments indicated that solutions of glyoxal and/or methylglyoxal did not form films without the presence of propanal (ultimately confirmed by these survey experiments), concentrations of mixed organics were chosen to keep the propanal concentration constant, so that any differences in film formation rates in the mixtures compared to propanal alone could not simply be due to a different concentration of propanal and therefore would indicate that glyoxal and/or methylglyoxal could impact the ability of propanal to form films. This results in samples that have a total organic concentration that increases with the number of organics present up to 0.09 M for solutions that contain all three organics.”

Second, the second sentence in Section 3.4 (P28586, L23-25) was revised as shown in blue below to clarify that observed increases in film formation rates when glyoxal is present are likely due to an increase in organic reactants available for film-formation reactions (i.e. an increase in the organic loading). It now reads as follows:

“Although glyoxal and methylglyoxal did not form films in the absence of propanal, the mixtures of 0.03 M propanal and 0.03 M glyoxal formed films faster than 0.03 M propanal alone suggesting that products of cross-reactions between glyoxal and propanal participate in film formation, resulting in faster film formation due to higher total concentrations of reactants available for film-forming reactions. In contrast, mixtures of 0.03 M propanal and 0.03 M methylglyoxal formed films more slowly than 0.03 M propanal alone.”

P28578, L1-4: Were any steps taken by the authors to ascertain if the composition of the film generated from a mixture of 0.30 M propanal and sulfuric acid was equivalent to that generated from a mixture of 0.030 M propanal and sulfuric acid? The latter concentration is remarked in P28577, L11-14 as being more atmospherically relevant. Also, were any measurements taken to compare the composition of the films formed under the different environmental conditions studied (temperature/illumination)? The measurements performed at -19 °C will be the most atmospherically relevant. Chemical analysis was performed for 0.30 M propanal solutions since our 0.030 M solutions had not produced a sufficient quantity of film for removal without substantial contamination by the underlying sulfuric acid solution which prohibited spectral analysis. However, after many trials we were able to extract enough film from one 0.030 M propanal sample to obtain an NMR spectrum that, although weak, nevertheless allows identification of major film species (see new Section 3.3 added to the manuscript and shown below for details). We thank the referee for inspiring us to redouble our efforts to address this important point.

NMR spectra of films formed in the dark and at 0°C show the presence of the same major species as the films formed under fluorescent light at room temperature along with some differences in their relative peak ratios at 0°C (see text added to the manuscript below for details). (Unfortunately, solutions stored at -19°C did not produce a sufficient quantity of film for removal and analysis without contamination by the underlying sulfuric acid solution.)

These results are related to some aging results requested by Referee #3 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 % H₂SO₄ as a starting point, since surface films were only formed on solutions containing propanal and since propanal formed films fastest at 48 wt % H₂SO₄. 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.”

P28579, L19 to P28580, L2: Please elaborate further on the statement that there was variability in film formation rates between replicates of the survey experiments. How consistent were the data? It would also be helpful to have further details on the actual rate of film growth for the different aldehyde mixtures under the various conditions of pH/temperature/illumination. This could be reported in terms of whatever metric the authors used to quantify it, however it would give the reader an appreciation as to whether stated differences in rate were on the order of minutes, days, months etc. Such data could be included in the Supplementary Information.

We have added the requested film formation rate data to the Supplement in the form of graphs of time required to form visible films as a function of acidity for each of the various organic mixtures (Figures S5 and S6). These graphs also provide data on variability since 3 replicate sets

of experiments are presented. Further details about film formation rates and the likely origin of the variability is also provided in the text as shown in blue below:

“There was variability in film formation rates for replicates of the survey experiments most likely due to differences in the gentle movement of the samples that was required to detect films during daily visual observations; however, the following general trends emerged (see Figs. S5 and S6 in the Supplement for trends and variability). First, the precise dependence of film-formation rate on acidity was complex, but, in general, the films formed faster at higher acidity, consistent with acid-catalyzed processes. In fact, the most acidic (76 wt % H₂SO₄) propanal/glyoxal mixture produced a surface film immediately upon combining the reactants, although the other organic mixtures formed films more slowly at 76 wt % than at 48 wt % H₂SO₄. Specifically, films were first observed on propanal-only samples after 4 days in 48 wt % H₂SO₄, versus 5-10 days in 76 wt % H₂SO₄; and visible film formation on propanal/methylglyoxal and propanal/glyoxal/methylglyoxal samples required 5-22 days in 48 wt % H₂SO₄, while samples in 76 wt % H₂SO₄ still did not have visible films after 180 days. Second, film-formation rates also varied as a function of organic mixture. In general, most mixtures containing glyoxal formed films more rapidly than those without, while mixtures containing methylglyoxal consistently formed films more slowly whenever there was a detectable difference in rates (see Figure S6 in the Supplement). Third, films formed both in the dark and under fluorescent light with no consistent trend in formation rate. Finally, films formed days to months more slowly at colder temperatures, but, importantly for application to the cold UT/LS, were eventually observed (after approximately 100 days) even at the lowest temperature (-19°C) examined.”

Figure S1. The left hand image is extremely difficult to make out, even with the explanation given in the caption. I think this image either needs to be replaced with a clearer picture or removed.

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