

1 **Complex chemical composition of colored surface films**
2 **formed from reactions of propanal in sulfuric acid at upper**
3 **troposphere/lower stratosphere aerosol acidities**

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10
11 **Abstract**

12 Particles in the upper troposphere and lower stratosphere (UT/LS) consist mostly of concentrated
13 sulfuric acid (40-80 wt %) in water. However, airborne measurements have shown that these
14 particles also contain a significant fraction of organic compounds of unknown chemical
15 composition. Acid-catalyzed reactions of carbonyl species are believed to be responsible for
16 significant transfer of gas phase organic species into tropospheric aerosols and are potentially
17 more important at the high acidities characteristic of UT/LS particles. In this study, experiments
18 combining sulfuric acid (H₂SO₄) with propanal and with mixtures of propanal with glyoxal
19 and/or methylglyoxal at acidities typical of UT/LS aerosols produced highly colored surface
20 films (and solutions) that may have implications for aerosol properties. In order to identify the
21 chemical processes responsible for the formation of the surface films, Attenuated Total
22 Reflectance – Fourier Transform Infrared and ¹H Nuclear Magnetic Resonance spectroscopies
23 were used to analyze the chemical composition of the films. Films formed from propanal were a
24 complex mixture of aldol condensation products, acetals and propanal itself. The major aldol
25 condensation products were the dimer (2-methyl-2-pentenal) and 1,3,5-trimethylbenzene, which
26 was formed by cyclization of the linear aldol condensation trimer. Additionally, the strong
27 visible absorption of the films indicates that higher order aldol condensation products must also
28 be present as minor species. The major acetal species were 2,4,6-triethyl-1,3,5-trioxane and
29 longer-chain linear polyacetals which are likely to separate from the aqueous phase. Films
30 formed on mixtures of propanal with glyoxal and/or methylglyoxal also showed evidence for

31 products of cross-reactions. Since cross-reactions would be more likely than self-reactions under
32 atmospheric conditions, similar reactions of aldehydes like propanal with common aerosol
33 organic species like glyoxal and methylglyoxal have the potential to produce significant organic
34 aerosol mass and therefore could potentially impact chemical, optical and/or cloud-forming
35 properties of aerosols, especially if the products partition to the aerosol surface.

36

37 **1 Introduction**

38 Aerosols in the upper troposphere and lower stratosphere (UT/LS) are composed primarily of
39 sulfuric acid (40-80 wt %) (Clegg et al., 1998; Finlayson-Pitts and Pitts, 2000; Tabazadeh et al.,
40 1997) and water but they also contain significant fractions of organic compounds (Froyd et al.,
41 2009; Murphy et al., 2007; 2014; 1998). In the case of UT aerosols, the amount of organic
42 material can even exceed the amount of sulfate present (Murphy et al., 1998). The potential
43 impacts of this organic material on chemical, optical and cloud-forming properties of UT/LS
44 aerosols are highly uncertain since relatively little is known about the chemical composition of
45 the organic fraction because available sampling techniques and frequencies are limited by the
46 high altitude airborne missions required.

47 In contrast to UT/LS aerosols, tropospheric aerosols are better sampled so it is well
48 established that they contain major fractions of organics (up to 90 %) (e.g., Calvo et al., 2013;
49 Hallquist et al., 2009; Jacobson et al., 2000; Jimenez et al., 2009; Kanakidou et al., 2005;
50 Murphy et al., 2006; Zhang et al., 2007), and there have been many studies aimed at chemical
51 characterization of tropospheric organic aerosol (OA) particles and at determining the
52 physical/chemical pathways for the formation of OA. In particular, reactions of carbonyl-
53 containing organic species including aldol condensation, hemiacetal/acetal formation,
54 organosulfate formation and various polymerization reactions have all been identified as
55 potential sources of low-volatility organic products in tropospheric organic aerosols (Barsanti
56 and Pankow, 2004; Ervens and Volkamer, 2010; Gao et al., 2004; Garland et al., 2006; Holmes
57 and Petrucci, 2007; Jang et al., 2002; 2004; Kalberer et al., 2004; Liggio and Li, 2006; 2008;
58 Liggio et al., 2007; Lim et al., 2010; Michelsen et al., 2004; Nozière and Esteve, 2007; Nozière
59 and Riemer, 2003; Sareen et al., 2010; Shapiro et al., 2009; Surratt et al., 2007; 2006; Tan et al.,
60 2010; Tolocka et al., 2004; Zhao et al., 2005; Ziemann and Atkinson, 2012). Since these

61 reactions are all either acid-catalyzed or require sulfate, they are likely to be even more favorable
62 at the high sulfuric acid concentrations typical of UT/LS aerosols.

63 Preliminary experiments for the current work, in which various carbonyl species (propanal,
64 glyoxal and/or methylglyoxal) were combined with highly concentrated sulfuric acid to simulate
65 UT/LS aerosol acidities, produced highly colored solutions; and solutions containing propanal
66 produced reaction products that partitioned to the liquid surface as macroscopic semi-solid
67 surface films that were also highly colored. The possibility that similar organic products could
68 partition to thin layers or films on the surface of UT/LS aerosols is of particular interest because
69 organic compounds that coat aerosol particles would have the most dramatic effects on aerosol
70 chemical, optical and/or cloud-forming properties (see Donaldson and Vaida (2006) and McNeill
71 et al. (2013) for reviews of aerosol surface coatings and their impacts on aerosol properties). For
72 example, organic coatings on aqueous droplets and sulfuric acid aerosols have been observed to
73 impede water uptake and/or evaporation in laboratory experiments (e.g., Davies et al., 2013;
74 Otani and Wang, 1984; Rubel and Gentry, 1984; Seaver et al., 1992; Xiong et al., 1998), so
75 organic coatings on UT/LS aerosols and/or droplets could potentially inhibit water condensation
76 and therefore cloud formation and/or growth. Organic coatings may also impact heterogeneous
77 reactions at aerosol surfaces; for example, reactive uptake of N_2O_5 has been shown to be
78 impeded by various organic coatings which could reduce the rate of hydrolysis of N_2O_5 to HNO_3
79 on sulfuric acid aerosols, affecting NO_x and OH budgets (Anttila et al., 2006; Badger et al.,
80 2006; Cosman and Bertram, 2008; Cosman et al., 2008; Escorcia et al., 2010; Evans and Jacob,
81 2005; Folkers et al., 2003; Gaston et al., 2014; Knopf et al., 2007; McNeill et al., 2006; Park et
82 al., 2007; Riemer et al., 2009; Thornton and Abbatt, 2005). Similarly, organic coatings on sulfate
83 aerosols would alter optical properties, especially if the organics are highly absorbing in the UV-
84 visible. In order to assess whether species that form surface films on propanal/ H_2SO_4 mixtures in
85 the laboratory could be important in UT/LS aerosols, the reactions responsible for film formation
86 must be identified, which is, therefore, the focus of the present work.

87 Recent work with various other aldehydes (Li et al., 2011; Sareen et al., 2010; Schwier et al.,
88 2010) demonstrated that products of reactions of formaldehyde, acetaldehyde, glyoxal,
89 methylglyoxal and their mixtures are surface-active even in water and ammonium sulfate/water
90 solutions characteristic of less acidic lower tropospheric aerosols. Their chemical

91 characterization of the reaction products identified hemiacetal oligomers and aldol condensation
92 products, but the surface-active species were not specifically identified.

93 In order to identify the chemical species present in films formed by propanal and sulfuric
94 acid, we consider the products of the following potential reactions (identified by a letter in Fig.
95 1): (A) aldol condensation, (B) trimethylbenzene formation via cyclization of the linear trimer
96 produced by aldol condensation, (C) hemiacetal, acetal, and/or polyacetal formation, (D)
97 trioxane formation via cyclotrimerization and (E) organosulfate formation. Each of these
98 processes result in higher molecular weight products, which could result in partitioning to the
99 solid phase as a surface film.

100 Aldol condensation products are expected since it can be seen from Fig. 1 that they are the
101 only potential products containing sufficient conjugation to absorb visible light, but they are not
102 necessarily the major component of the films since only tiny amounts of such chromophores are
103 necessary for color (McLaren, 1983). Products of propanal aldol condensation reactions have
104 been observed in aqueous media containing various catalysts including anion exchange resin
105 (Pyo et al., 2011), ammonium and carbonate salts (Nozière et al., 2010), mixed metal oxides
106 (Tichit et al., 2002), and zeolites (Hoang et al., 2010). In the case of zeolite catalysts, 1,3,5-
107 trimethylbenzene was also observed and proposed to form from the linear trimer produced by
108 aldol condensation reactions (Fig. 1b). Aldol condensation reactions of propanal have also been
109 studied in concentrated sulfuric acid (60-96 wt %) solutions by Noziere and Esteve (2007) and
110 Casale et al. (2007). Noziere and Esteve reported the UV-vis spectra of aldol condensation
111 products of 6 carbonyl compounds including propanal and concluded that their absorption index
112 could become significant over the approximately two-year residence time of stratospheric
113 aerosols. Casale et al. measured bulk reaction rates for a series of aliphatic aldehydes ($C_2 - C_8$),
114 showing that butanal and propanal had the highest reaction rates, but concluding that the rates
115 were not fast enough to be responsible for transfer of significant organic mass into tropospheric
116 aerosols. Both studies focused on aldol condensation reactions due to their potential to form light
117 absorbing compounds and therefore used UV-visible spectroscopy for product detection, which
118 is not sensitive to products of the other potential reactions (C-E) considered here.

119 Propanal may also undergo acid-catalyzed reactions with its hydrated form (diol) to form
120 hemiacetals, acetals and/or linear polyacetals as shown in Fig. 1c. In addition to these linear
121 species, propanal may also undergo acid-catalyzed cyclotrimerization to form a cyclic polyacetal

122 (a trioxane) (Fig. 1d). These reactions have not been reported specifically for propanal in sulfuric
123 acid, but Garland et al. (2006) have shown that sulfuric acid aerosols exposed to hexanal vapor
124 contained hemiacetals while Li et al. (2008) identified a trioxane in bulk reactions of octanal
125 with sulfuric acid but not in sulfuric acid aerosols exposed to octanal vapor. (In both studies,
126 aldol condensation products were also observed.) Furthermore, propanal has been shown to form
127 a trioxane in aqueous solution (Corrochano et al., 2010) and to form a mixture of aldol
128 condensation products, hemiacetals and acetals in the presence of an anion-exchange resin
129 catalyst (Pyo et al., 2011).

130 Lastly, alcohols may react with sulfuric acid to form sulfate esters (Deno and Newman, 1950;
131 Iraci et al., 2002; Michelsen et al., 2006; Minerath et al., 2008; Van Loon and Allen, 2004; 2008;
132 Vinnik et al., 1986), so alcohol species including the diol formed by hydration of propanal and/or
133 (hemi)acetals (Surratt et al., 2008) formed from propanal (Fig. 1c) could react directly with
134 sulfuric acid to form organosulfates similar to those formed by reaction of glyoxal on sulfuric
135 acid aerosols (Liggio et al., 2005). An example is shown for reaction of the propanal hydrate in
136 Fig. 1e.

137 In the present study we first employ a combination of Attenuated Total Reflectance – Fourier
138 Transform Infrared (ATR-FTIR) and ^1H Nuclear Magnetic Resonance (^1H NMR) spectroscopies
139 to identify the major species in the films formed by propanal on sulfuric acid solutions. In order
140 to approach more atmospherically-realistic mixtures of organics and to address the possibility of
141 cross-reactions between different carbonyl species, we also examined films formed on mixtures
142 of propanal with glyoxal and/or methylglyoxal. Finally, we also used UV-visible spectroscopy of
143 the liquid solutions to gain chemical insight into the identity of the chromophores and to
144 illustrate their potential importance for UT/LS aerosol optical properties.

145

146 **2 Experimental methods**

147 Surface films were first detected on solutions of propanal and its mixtures with glyoxal and/or
148 methylglyoxal in sulfuric acid that were allowed to react for several weeks (see Fig. S1 in the
149 Supplement for photos of typical surface films). Subsequently, controlled survey studies were
150 performed to examine the conditions required for formation of surface films. In these
151 experiments, samples of propanal, glyoxal, and/or methylglyoxal in all possible combinations of
152 1, 2 or all 3 species (0.030 M in each organic present) were prepared in stock solutions of 19, 37,

153 48 and 76 wt % sulfuric acid (H₂SO₄). Since initial experiments indicated that solutions of
154 glyoxal and/or methylglyoxal did not form films without the presence of propanal (ultimately
155 confirmed by these survey experiments), concentrations of mixed organics were chosen to keep
156 the propanal concentration constant, so that any differences in film formation rates in the
157 mixtures compared to propanal alone could not simply be due to a different concentration of
158 propanal and therefore would indicate that glyoxal and/or methylglyoxal could impact the ability
159 of propanal to form films. This results in samples that have a total organic concentration that
160 increases with the number of organics present up to 0.09 M for solutions that contain all three
161 organics. Although UT/LS aerosol concentrations of these organic compounds are unknown,
162 0.03 M is likely much larger than UT/LS concentrations of any one carbonyl species, but is more
163 reasonable if considered as representative of the total aldehyde or carbonyl concentration.
164 Sulfuric acid stock solutions were prepared by dilution of concentrated sulfuric acid (96-98 wt
165 %, Sigma-Aldrich, ACS grade) with Milli-Q water, and concentrations were confirmed by
166 titration with standardized sodium hydroxide (0.5 N, Sigma-Aldrich). The following Sigma-
167 Aldrich organics were used: 97 wt % reagent grade propanal, 40 wt % glyoxal and 40 wt %
168 methylglyoxal in water. 4.0 mL aliquots of each mixture were transferred to multiple 8 mL glass
169 vials and stored under each of the following temperature and lighting conditions: room
170 temperature (21-24°C)/constant fluorescent light, room temperature/dark, 0°C/dark, -19°C/dark.
171 Samples were visually monitored daily for color changes and formation of surface films in order
172 to survey which mixtures formed films and to assess the impact of acidity, organic mixture,
173 temperature and fluorescent light on film formation rates.

174 Chemical analysis of the films required production of films in sufficient quantity to allow
175 physical removal of a portion without disturbing the underlying sulfuric acid solutions and
176 thereby avoiding spectroscopic interferences from water and sulfuric acid. Therefore, samples
177 used for chemical analysis were prepared as above, except at the higher concentration of 0.30 M
178 in each organic and were stored in volumetric flasks (room temperature/fluorescent light) which
179 caused the film to concentrate on the small liquid surface area in the neck of the flask. Film
180 samples were removed and transferred with a glass rod to the surface of an ATR crystal for
181 analysis by FTIR spectroscopy. ATR-FTIR spectra of the films and standards were collected on
182 a Nicolet 6700 spectrophotometer from 4000-700 cm⁻¹ at 1cm⁻¹ resolution using an MCT
183 detector, and a 10-bounce AMTIR ATR crystal with 45 degree mirrors from PIKE. ATR-FTIR

184 was chosen for chemical analysis since the semi-solid films could be directly analyzed on a
185 crystal compatible with concentrated sulfuric acid and without any need to alter the chemical
186 environment by dissolving the sample in a solvent. In order to provide more chemical specificity,
187 films were also analyzed by ^1H NMR spectroscopy using a Varian INOVA 400 MHz
188 spectrometer. NMR samples were prepared by dissolving film samples in deuterated chloroform
189 (CDCl_3) in quartz NMR tubes (5 mm outer diameter). ATR-FTIR and/or NMR spectra were also
190 recorded for the following commercially available standards: 2-methyl-2-pentenal (97 wt %
191 Sigma-Aldrich), 1,3,5-trimethylbenzene and 2,4,6-triethyl-1,3,5-trioxane (AKos GmbH, custom
192 synthesis).

193 Finally, the UV-visible absorption spectra of solutions (0.030 M in each organic) were
194 obtained using a Varian Cary 50 Bio UV/visible spectrometer with a diode array detector and
195 quartz cuvettes of various pathlengths from 0.01–10 mm for different regions of the spectrum.
196 Prior to analysis, solutions were filtered through 2.5 μm Teflon filters to remove any suspended
197 solid particulates.

198

199 **3 Results**

200 **3.1 Formation of organic surface films**

201 Carbonyl-containing organics (propanal, glyoxal and/or methylglyoxal) mixed with sulfuric acid
202 (19-76 wt %) to simulate UT/LS aerosol acidities produced colored solutions, precipitates and
203 surface films. At the highest acidities, all individual organics and organic mixtures examined
204 (0.030 M in each organic) produced visibly colored solutions that darkened with time. Mixtures
205 containing propanal produced the most deeply colored solutions, progressing from yellow to
206 orange to red to brown over timescales ranging from minutes to months. This color darkening
207 progressed faster at higher acidities, consistent with an acid-catalyzed reaction. Many propanal-
208 containing mixtures also eventually produced colored precipitates and/or surface films.

209 (Mixtures containing only glyoxal and/or methylglyoxal did not produce surface films.) These
210 solids or semi-solids were observed either as particles suspended in the liquid (usually collecting
211 near the surface) and/or as semi-rigid macroscopic films on the surface. In principle, the films
212 could potentially be formed either by heterogeneous reactions at the air/liquid interface or by
213 liquid-phase reactions resulting in products that partition to the surface. The latter process,
214 however, is supported by the observation that when solutions were stored in volumetric flasks

215 solid, dark colored material sometimes collected on the upper slanted walls in the body of the
216 flask before migrating to the surface; presumably the material rose due to its low density relative
217 to the solution, but was temporarily impeded from reaching the surface by the flask walls.
218 Furthermore, the quantity of film material observed cannot be easily explained by heterogeneous
219 surface reactions alone.

220 There was variability in film formation rates for replicates of the survey experiments
221 most likely due to differences in the gentle movement of the samples that was required to detect
222 films during daily visual observations; however, the following general trends emerged (see Figs.
223 S5 and S6 in the Supplement for trends and variability). First, the precise dependence of film-
224 formation rate on acidity was complex, but, in general, the films formed faster at higher acidity,
225 consistent with acid-catalyzed processes. In fact, the most acidic (76 wt % H₂SO₄)
226 propanal/glyoxal mixture produced a surface film immediately upon combining the reactants,
227 although the other organic mixtures formed films more slowly at 76 wt % than at 48 wt %
228 H₂SO₄. Specifically, films were first observed on propanal-only samples after 4 days in 48 wt %
229 H₂SO₄, versus 5-10 days in 76 wt % H₂SO₄; and visible film formation on
230 propanal/methylglyoxal and propanal/glyoxal/methylglyoxal samples required 5-22 days in 48
231 wt % H₂SO₄, while samples in 76 wt % H₂SO₄ still did not have visible films after 180 days.
232 Second, film-formation rates also varied as a function of organic mixture. In general, most
233 mixtures containing glyoxal formed films more rapidly than those without, while mixtures
234 containing methylglyoxal consistently formed films more slowly whenever there was a
235 detectable difference in rates (see Figure S6 in the Supplement). Third, films formed both in the
236 dark and under fluorescent light with no consistent trend in formation rate. Finally, films formed
237 days to months more slowly at colder temperatures, but, importantly for application to the cold
238 UT/LS, were eventually observed (after approximately 100 days) even at the lowest temperature
239 (-19°C) examined.

240

241 **3.2 Chemical composition of surface films**

242 The highly-colored nature of the surface films (only formed on solutions containing propanal) is
243 strong evidence for aldol condensation products, as aldol condensation is the only potential
244 reaction (Fig. 1) of propanal in sulfuric acid that can result in products with the conjugation
245 required to cause absorption of visible light. In fact, multiple aldol condensation steps are

246 required to produce sufficient conjugation, since the first aldol condensation product of propanal
247 (2-methyl-2-pentenal, see Fig. 1a) is colorless with λ_{max} for the $\pi \rightarrow \pi^*$ transition of ~ 266 nm
248 and ~ 233 nm in 75 wt % H_2SO_4 (Casale et al., 2007) and water (our standard), respectively.
249 Further conjugation from additional aldol condensation reactions of 2-methyl-2-pentenal with
250 propanal or with itself is required to shift absorption into the visible. Although products from
251 multiple aldol condensation steps are almost certainly responsible for the film color, these
252 chromophores are not necessarily the major chemical components of the films, so ATR-FTIR
253 and ^1H NMR spectroscopies were used to analyze the chemical composition of the surface films.
254 The combined results of these two techniques provide evidence that the films are a mixture of
255 aldol condensation products (mainly 2-methyl-2-pentenal and 1,3,5-trimethylbenzene) and
256 acetals (mainly 2,4,6-triethyl-1,3,5-trioxane and longer-chain linear polyacetals) as detailed in
257 Sects. 3.2.1 through 3.2.3 below. The detailed chemical analysis in these sections is presented for
258 surface films formed on 0.30 M propanal/48wt % H_2SO_4 as a starting point, since surface films
259 were only formed on solutions containing propanal and since propanal formed films fastest at 48
260 wt % H_2SO_4 . These films were stored at room temperature under constant fluorescent light and
261 were sampled and analyzed 7 days after mixing the solutions. Sections 3.3-3.5 subsequently
262 address the impact of varying the temperature, illumination, organic concentration, film age,
263 acidity and organic mixture from this base case.

264

265 **3.2.1 Aldol condensation products**

266 Figure 2 presents a typical ATR-FTIR spectrum of a surface film formed on a 7-day old 0.30 M
267 propanal/48wt % H_2SO_4 mixture (in green) along with spectra of four standards for comparison.
268 The strong absorption band in the film spectrum at 1689 cm^{-1} and the band at 1643 cm^{-1} are
269 consistent with the characteristic C=O and C=C stretching vibrations, respectively, of an α,β -
270 unsaturated aldehyde, which is produced by aldol condensation (Fig. 1a). The spectrum of neat
271 2-methyl-2-pentenal shown in Fig. 2 (blue) displays these bands at 1687 and 1643 cm^{-1} and is
272 scaled to illustrate the maximum amount of the film spectrum that could be explained by its
273 presence (limited by the size of the C=C band at 1643 cm^{-1}). An additional C=O peak at 1722
274 cm^{-1} occurs in the unsaturated aldehyde stretching region and is assigned to unreacted propanal.
275 In Fig. 2, the spectrum of neat propanal (red) is also scaled to illustrate its potential contribution
276 to the spectrum of the film.

277 The ^1H NMR spectrum for this film presented in Fig. 3 indicates that 2-methyl-2-pentenal is
278 the dominant species since it contains strong peaks (assigned in Fig. 3) corresponding to all five
279 types of hydrogens in 2-methyl-2-pentenal in the correct multiplicity and within 0.03 ppm of our
280 standard. Although some of the peaks are too small or too close to interfering peaks to integrate
281 reliably, the relative peak intensities are also roughly consistent with the standard. Residual
282 propanal is similarly positively identified by comparison to the standard as shown by peak
283 assignments in Fig. 3. There are no additional detectable NMR peaks consistent with linear
284 compounds with additional units of conjugation due to multiple aldol condensation steps,
285 indicating that they must be significantly less abundant than 2-methyl-2-pentenal and therefore
286 will not contribute substantially to the FTIR spectrum, either. (For example, the protons labelled
287 A and B in 2,4-dimethyl-2,4-heptadienal (Fig. 1) would be expected to appear as singlets with
288 chemical shifts near those for 2,4-hexadienal (Spectral Database for Organic Compounds, 2014
289 (SDBS)) at 9.5 and 7.1 ppm, respectively.)

290 Although there is no NMR evidence for linear aldol condensation products beyond 2-methyl-
291 2-pentenal, NMR peaks at 2.26 and 6.79 ppm confirm the presence of 1,3,5-trimethylbenzene
292 (mesitylene) (SDBS), which has previously been observed to form in reactions of propanal over
293 acidic zeolite catalysts (Hoang et al., 2010). Hoang et al. proposed that 1,3,5-trimethylbenzene
294 was formed by acid-catalyzed cyclization and subsequent dehydration of the trimer formed by
295 aldol condensation (2,4-dimethyl-2,4-heptadienal) of propanal as shown in Fig. 1b, which is a
296 reasonable mechanism for sulfuric acid solutions as well. Furthermore, the trimer formed by
297 aldol condensation of acetone has also been shown to cyclize to form 1,3,5-trimethylbenzene in
298 sulfuric acid (Duncan et al., 1998; Kane et al., 1999; Klassen et al., 1999). In Fig. 2, the ATR-
299 FTIR spectrum of neat 1,3,5-trimethylbenzene (black) is scaled to the film spectrum to indicate
300 its maximum potential contribution. The comparison shows that the film spectrum is consistent
301 with the presence of some 1,3,5-trimethylbenzene in the film since it has bands corresponding to
302 the two most intense 1,3,5-trimethylbenzene bands at 834 and 1609 cm^{-1} , the latter of which lies
303 in the region for aromatic skeletal vibrations and, therefore, cannot be explained by any other
304 potential products.

305 Although 2-methyl-2-pentenal and 1,3,5-trimethylbenzene are shown here to be the major
306 products resulting from aldol reactions, both are colorless, so the more highly conjugated
307 compounds formed by further aldol condensation steps that are presumably responsible for the

308 film color must be minor constituents. Therefore, there must also be additional compounds
309 present in the film to explain the strength of the peaks that appear in the FTIR spectrum between
310 1500-800 cm^{-1} and 3000-2800 cm^{-1} .

311

312 **3.2.2 Ethers: acetals/hemiacetals and linear/cyclic polyacetals**

313 In addition to aldol condensation products, the FTIR and NMR spectra both also display
314 evidence for ether groups (C-O-C) due to strong peaks in the 1200-1000 cm^{-1} region of the FTIR
315 spectrum (Fig. 2) and peaks in the 4.5-5.1 ppm region of the NMR spectrum. Species that could
316 be responsible for these ether signatures include hemiacetals, acetals and/or higher order
317 polyacetal polymers which can form from the reaction of propanal with one or more of its
318 hydrates (diols) (Fig. 1c) or from cyclo-trimerization of propanal to form the cyclic acetal, 2,4,6-
319 triethyl-1,3,5-trioxane (Fig. 1d). Of these potential products, the cyclotrimer is most easily
320 confirmed since it is readily identified by comparison of the FTIR and NMR spectra of the film
321 to the spectra of 2,4,6-triethyl-1,3,5-trioxane as indicated by the peaks assigned to the trioxane
322 (T) in Figs. 2 and 3. Specifically, the ^1H NMR spectrum of the film contains all three of the
323 peaks in the reference spectrum (SDBS): a triplet at 4.78 ppm, a complex multiplet at 1.67 ppm
324 and a triplet at 0.94 ppm (although the broad peak group at 0.94 ppm can only be partially due to
325 the trioxane due to its strong intensity relative to the other trioxane peaks). Similarly, as shown
326 by assignments in Fig. 2, at least 13 peaks in the FTIR spectrum of the film correspond to peaks
327 in the spectrum of neat 2,4,6-triethyl-1,3,5-trioxane (including all 6 of the strongest peaks
328 between 1500-900 cm^{-1}). Furthermore, previous studies of 2,4,6-triethyl-1,3,5-trioxane report
329 that it phase separates upon formation from propanal/catalyst solutions (Sato et al., 1993; 1991),
330 consistent with our surface film formation.

331 Upon assignment of the cyclotrimer peaks, only one major peak in the FTIR spectrum of the
332 film remains unexplained by species identified thus far (2,4,6-triethyl-1,3,5-trioxane, 2-methyl-2-
333 pentenal, 1,3,5-trimethylbenzene and propanal). This peak at 945 cm^{-1} is, however, the strongest
334 peak in the spectrum of the film and therefore, must be a major peak in the spectrum of the
335 absorbing species. The hemiacetal and single acetal formed by propanal (Fig. 1c) are unlikely to
336 be responsible for the peak at 945 cm^{-1} since they would be expected to produce their strongest
337 bands at higher frequencies. Specifically, the hemiacetal would produce a strong FTIR
338 absorption band in the 1150-1085 cm^{-1} region from the asymmetric stretch of its single ether

339 group, while the acetal contains the C-O-C-O-C moiety which would produce 5 characteristic
340 bands between 1200-1020 cm^{-1} (Bergmann and Pinchas, 1952). Furthermore, both the hemiacetal
341 and acetal are also unlikely to be major ether constituents since only a weak peak exists in the
342 OH stretching region (3500-3400 cm^{-1}) where a stronger peak (with respect to the peaks in the
343 ether region) would be expected due to the OH groups.

344 Instead, the strong peak at 945 cm^{-1} most likely results from longer-chain polymers of
345 propanal (polyacetal in Fig. 1c) due to -C-O-C-O-C- stretching bands that are shifted to lower
346 frequencies with the addition of additional ether groups. Spectra of polymers of various small
347 aldehydes (formaldehyde, acetaldehyde and propanal) which contain the same polymethoxy (-C-
348 O-)_n backbone display only very weak OH stretching bands but multiple very strong, broad,
349 overlapping absorption bands between 925-975 cm^{-1} (Novak and Whalley, 1959a, b, 1962; Vogl,
350 1964a, b). Although the peak at 945 cm^{-1} does not exactly match any of the three strongest peaks
351 (975, 960 and 925 cm^{-1}) in this region in the Novak and Whalley (1959a) spectrum of the
352 polymethoxy polymer formed by pressurization of propanal, there is such broad absorption in the
353 entire 980-920 cm^{-1} region of the polymer spectrum that a peak near 945 cm^{-1} may not be
354 distinguishable. Furthermore, the polymer present in our surface film is likely to display different
355 relative intensities of the peaks in this region due to differences in degree of polymerization
356 and/or differences in relative quantities of rotational isomers (Novak and Whalley, 1959a).
357 Additionally, bands may also be shifted in frequency due to different interactions between
358 polymer chains (Novak and Whalley, 1959a) in the complex surface film matrix. Finally, the
359 NMR spectrum of the film is also consistent with the presence of propanal polymer since the 4.5-
360 5.1 ppm region contains multiple unassigned peaks consistent with ethers and similar to the
361 broad group of unresolved peaks from 4.5-5.0 ppm that characterizes the NMR spectrum of the
362 polymethoxy polymer formed by acetaldehyde (Vogl, 1964a), while CH₂ and CH₃ protons from
363 the ethyl chains are likely responsible for peaks in the 1.0-1.7 ppm region and for a portion of the
364 triplet at 0.94 ppm, respectively.

365 After this identification of polymers of propanal, we note that all of the major bands in the
366 infrared spectrum that could not be explained by aldol condensation products either correspond
367 to 2,4,6-triethyl-1,3,5-trioxane or could reasonably be assigned to longer-chain linear propanal
368 polymers.

369

370 **3.2.3 Other potential film components: organosulfates, etc.**

371 In order to test for the presence of organosulfates, reaction mixtures were prepared with
372 hydrochloric acid at the same pH as the sulfuric acid mixtures. The formation of surface films on
373 these mixtures demonstrates that organosulfates are not necessary for film formation, and the
374 similarity of the ATR-FTIR spectra for films formed on sulfuric acid and hydrochloric acid
375 solutions (example shown in Fig. 4 for 0.30 M propanal/48 wt % H₂SO₄) demonstrates that
376 organosulfates are not present in significant quantities. We note, however, that organosulfates
377 could still be produced in the sulfuric acid solutions, where they would be expected to remain
378 due to their ionizability.

379 Although all of the major peaks (and many of the minor peaks) in both the FTIR and NMR
380 spectra of the film can be assigned to the chemical species discussed thus far, some small
381 unassigned peaks (e.g. NMR peaks at 3.2 and 3.9 ppm) indicate the presence of other minor
382 species. These could include products of multiple aldol condensation steps, aldols that have not
383 lost water through the condensation process (see Fig. 1), the hemiacetal and acetal formed by
384 propanal, other acetals that could also potentially be formed by reactions of aldol condensation
385 products with propanal, and/or products from oxidation of films by light/air.

386

387 **3.3 Effects of light exposure, temperature, propanal concentration and film age**

388 The preceding detailed chemical analyses were presented for the base case of a film formed on a
389 7 day old solution of 0.30 M propanal in 48 wt % sulfuric acid, stored at room temperature under
390 fluorescent room light. Very similar NMR spectra were obtained from films formed on solutions
391 that were stored under different conditions (dark and/or 0°C), that were younger (1 and 4 days)
392 and older (68 and 134 days), or that were formed at lower propanal concentration (0.030 M); and
393 these spectra confirm the presence of the same major chemical species. Spectra of films formed
394 in the dark are not detectably different than those formed in the light, but films formed at
395 different ages, at 0°C, or at lower propanal concentration display the following significant
396 differences in relative peak areas between chemical species when compared to the base case.

397 There were two detectable trends in NMR peak area ratios with film age. First, the trioxane
398 (4.75 ppm) peak area decreased with age relative to all other species that produced peaks
399 separated well enough for integration [2-methyl-2-pentenal (9.39 ppm), trimethylbenzene (6.79
400 ppm) and propanal (9.79 ppm)]; furthermore, the oldest samples (68 and 134 days) lacked any

401 detectable trioxane. Trioxane peaks also decreased relative to the peaks in the ATR-FTIR spectra
402 assigned to long-chain polymers. Therefore, since trioxane decreases with time relative to all
403 other major film species and the films grow thicker with time, it is possible that trioxane is
404 initially formed rapidly, followed by slower formation of all other film species. Second, the
405 trimethylbenzene (6.79 ppm) to 2-methyl-2-pentenal (9.39 ppm) peak area ratio increased with
406 age (by a factor of 2 to 3 going from 1-7 day old samples to 68 and 134 day old samples). Since
407 2-methyl-2-pentenal is a precursor for trimethylbenzene formation, this result suggests that
408 trimethylbenzene formation continues beyond one week.

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

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

423

424 **3.4 Effect of acidity**

425 As discussed in Section 3.1, acidity has a complex effect on the formation rates of the surface
426 films that varies depending on the organic mixture. In general, films tended to form faster as the
427 acidity increased from 19 to 37 to 48 wt % H_2SO_4 , but films formed more slowly or not at all at
428 the highest acidity (76wt % H_2SO_4) in all mixtures except propanal/glyoxal. The FTIR spectra of
429 films formed on mixtures of 0.30 M propanal in 48 and 37 wt % H_2SO_4 solutions in Fig. 5
430 (shown in triplicate) demonstrate that there are also chemical differences in films formed at
431 different acidities. The spectra are scaled to the $\text{C}=\text{O}$ peak at 1690 cm^{-1} from aldol condensation

432 products (predominantly 2-methyl-2-pentenal) in order to illustrate differences in relative peak
433 intensities. Although there is considerable variability in relative peak intensities among the
434 spectra of replicates (most likely due to film inhomogeneity), the peaks in the 1200-900 cm^{-1}
435 region are generally larger relative to the C=O peak at the higher acidity (red), indicating a larger
436 relative contribution to the film from the 2,4,6-triethyl-1,3,5-trioxane and longer-chain polyacetal
437 polymers that absorb in this region. In addition, the films formed at the higher acidity also have
438 smaller peaks at 1608 cm^{-1} , indicating smaller concentrations of 1,3,5-trimethylbenzene relative
439 to aldol condensation products. Both of these trends are confirmed by NMR spectroscopy (data
440 not shown). The presence of more 2,4,6-triethyl-1,3,5-trioxane and polymers at higher acidities
441 is consistent with faster film formation at higher acidities in the 19-48 wt % H_2SO_4 range since
442 these species are most likely responsible for the phase separation into a surface film.
443 Additionally, slower film formation at the highest acidity (76 wt %) is potentially due to low
444 water content that reduces the formation of the diols required to begin the polymerization process
445 (see Fig. 1c).

446

447 **3.5 Cross-reactions with glyoxal and methylglyoxal**

448 To examine the potential effect of additional organic species with carbonyl groups on the
449 formation of films, mixtures of propanal with glyoxal and/or methylglyoxal were also examined.
450 Although glyoxal and methylglyoxal did not form films in the absence of propanal, the mixtures
451 of 0.03 M propanal and 0.03 M glyoxal formed films faster than 0.03 M propanal alone
452 suggesting that products of cross-reactions between glyoxal and propanal participate in film
453 formation, resulting in faster film formation due to higher total concentrations of reactants
454 available for film-forming reactions. In contrast, mixtures of 0.03 M propanal and 0.03 M
455 methylglyoxal formed films more slowly than 0.03 M propanal alone. A comparison of FTIR
456 spectra of films formed on various organic mixtures in 48wt % H_2SO_4 all prepared on the same
457 day are shown in Fig. 6. (Because significant variability in relative peak intensities exists in
458 replicate FTIR spectra of the films most likely due to inhomogeneity in the solid mixtures of
459 multiple chemical species, a complete set of replicate spectra are provided in the Supplement
460 (Figs. S3 and S4) to demonstrate that the differences between organic mixtures discussed here
461 are in fact due to differing chemical pathways and are not simply sampling artifacts.) The spectra
462 are again scaled to the C=O peak at 1690 cm^{-1} from propanal aldol condensation products in

463 order to illustrate differences between relative peak intensities. The spectra of the films from
464 propanal and propanal/glyoxal are nearly identical in the 1800-1600 cm^{-1} region indicating that
465 both films include 2-methyl-2-pentenal and unreacted propanal in similar ratios. Conversely, the
466 spectral pattern in the 1200-900 cm^{-1} region for the propanal/glyoxal film does not correspond to
467 the spectrum of 2,4,6-triethyl-1,3,5-trioxane as it does for the propanal-only film. Since glyoxal
468 did not form films by itself, this infrared signature is most likely due to products of cross
469 reactions between propanal and glyoxal.

470 The FTIR spectrum of the film from propanal and methylglyoxal deviates even farther from
471 that of propanal-only. Not only does it lack the signature of 2,4,6-triethyl-1,3,5-trioxane,
472 indicating products of cross-reactions, but, additionally, absorbance in the entire 1500-900 cm^{-1}
473 region is much stronger relative to the aldol condensation peak at 1690 cm^{-1} , indicating a
474 stronger relative contribution from acetal species. Finally, it is intriguing that 1) the spectrum of
475 the film formed on the propanal/glyoxal/methylglyoxal mixture is quite similar to that for the
476 propanal/methylglyoxal mixture, differing only in relative peak ratios (a result that remained true
477 even when the methylglyoxal concentration was reduced by up to a factor of 10, but not by a
478 factor of 100) and 2) that the rate of film formation was decreased from the rate for the
479 propanal/glyoxal mixture. This could indicate that glyoxal is somehow inhibited from
480 participating in film-forming reactions by the presence of methylglyoxal. The mechanism for
481 such inhibition is unclear, but plausible explanations include cross-reactions of glyoxal with
482 methylglyoxal that are faster than those with propanal, but that do not result in products that
483 partition to the film and/or dimerization reactions of propanal with methylglyoxal that are faster
484 than those with glyoxal, but that subsequently require more time to form polymers that are large
485 enough to partition into the film.

486

487 **3.6 UV-vis spectra of solutions**

488 Although the focus of this work is on characterization of the surface films, the UV-visible
489 absorption spectra of aged organic/sulfuric acid solutions were also examined in order to give
490 some insight into the potential formation of highly absorbing species over the long residence
491 time of lower stratospheric aerosols (~ 2 years). Figure 7a (purple) shows that a solution of 0.030
492 M propanal in 48 wt % sulfuric acid allowed to age for 274 days had two strong absorption peaks
493 around 200 and 245 nm most likely corresponding to species also observed in the films: 1,3,5-

494 trimethylbenzene and 2-methyl-2-pentenal, which absorb in water at ~200 and 234 nm,
495 respectively. More importantly, the absorbance extends significantly into the visible. There are
496 no other distinguishable peaks, but the absorbance is most likely due to overlapping peaks from
497 various longer oligomers formed by additional aldol condensation reactions of 2-methyl-2-
498 pentenal with propanal and/or with itself. Each sequential aldol condensation step would add
499 another unit(s) of conjugation and thereby shift the absorption peak to longer wavelengths. This
500 interpretation is supported by the observation that when the acidity was increased to 76 wt %
501 sulfuric acid (Fig. 1b), the intensity of the peak corresponding to 2-methyl-2-pentenal was
502 reduced (or even absent) and additional peaks became distinguishable at longer wavelengths
503 (270, 365, 388 (shoulder) and 458 nm). Nozière and Esteve (2007) observed a similar spectrum
504 for reaction products of propanal in 96 wt % sulfuric acid, and also ascribe these long
505 wavelength peaks to oligomers from aldol condensation reactions. Although they suggest that the
506 peak in their spectrum near 270 nm may be propanal itself, this cannot be the case for our
507 samples since the molar absorptivity of propanal is too small at $\sim 9 \text{ cm}^{-1} \text{ M}^{-1}$ (Xu et al., 1993).

508 The absorption spectra of mixtures of propanal with glyoxal and/or methylglyoxal are also
509 presented in Fig. 7. “Effective” molar absorptivities are calculated based only on the
510 concentration of the propanal reactant (0.030 M) so that any changes in absorbance (compared to
511 the propanal-only spectrum) must be due to the presence of the additional organic species. At
512 both acidities absorbance in most of the spectrum is increased, with methylglyoxal having a
513 larger effect than glyoxal, suggesting that the added organic species are undergoing aldol
514 condensation either via reactions with propanal or self-reactions. Although some of the
515 additional absorption may be due to glyoxal and methylglyoxal themselves, molar absorptivities
516 of these species are too small (Horowitz et al., 2001; Malik and Joens, 2000; Plum et al., 1983)
517 to contribute significantly at least below 350 nm.

518

519 **4 Discussion and atmospheric implications**

520 The major species present in surface films formed on bulk solutions of propanal in sulfuric acid
521 were identified as aldol condensation products (mainly 2-methyl-2-pentenal and 1,3,5-
522 trimethylbenzene) and polyacetals (mainly 2,4,6-triethyl-1,3,5-trioxane and longer-chain linear
523 polyacetals). Of these products, the polyacetal species (both cyclic and linear) are most likely to
524 be primarily responsible for the separation of the organic species from the solution into a

525 separate solid organic phase on the surface of the liquid due to their high molecular weight and
526 higher hydrophobicity compared to the two observed aldol condensation products. Since the
527 solid material in the laboratory samples rises to the surface of the solution due, at least in part, to
528 its low density relative to sulfuric acid, if similar insoluble acetals were formed from reactions of
529 aldehydes in liquid UT/LS aerosols, it is unclear whether they would exist as solid inclusions or
530 as surface coatings (full or partial), the latter of which would be more likely to alter aerosol
531 optical, chemical and/or cloud-nucleating properties.

532 Neither the solubility nor the reactive uptake coefficient of propanal in sulfuric acid has been
533 measured, but, based on the low concentration of propanal vapor in the UT/LS (~15 ppt at 11 km
534 and presumably much lower in the stratosphere (Singh et al., 2004)) and on the short lifetimes of
535 gas phase aldehydes with respect to photolysis, uptake and reaction of propanal alone to form
536 polyacetals is not expected to be a significant source of organic material in UT/LS aerosols.
537 However, polyacetal formation from aldehydes in general could be important for three reasons.
538 First, polyacetals may be formed from a variety of organic species since they have been observed
539 to form from many aliphatic aldehydes (Vogl, 2000) and have specifically been observed in
540 sulfuric acid for formaldehyde uptake (Iraci and Tolbert, 1997) and inferred for acetaldehyde
541 uptake (Williams et al., 2010). Second, the rate of film formation was greatly enhanced by the
542 presence of glyoxal, suggesting that carbonyl species already present in aerosols could enhance
543 the reactive uptake and polyacetal formation of small aldehydes, consistent with previous
544 experiments that demonstrated enhanced reactive uptake of acetaldehyde on sulfuric acid
545 solutions containing formaldehyde (Williams et al., 2010) and enhanced reactive uptake of
546 nonanal on mixed organic/sulfuric acid aerosols (Chan and Chan, 2011). Third, although aerosol
547 concentrations of any one aldehyde are unlikely to result in significant self-polymerization,
548 cross-reactions between aldehydes and/or between aldehydes and alcohols may be significant
549 and are specifically shown here to occur between propanal and two common aerosol organic
550 species (glyoxal and methylglyoxal).

551 Although uptake and dissolution of aldehydes onto sulfuric acid aerosols is the most likely
552 method of polyacetal formation directly from small volatile mono-aldehydes like propanal, there
553 may be more favorable methods for polyacetal formation in UT/LS aerosols. Since polyacetal
554 formation requires multiple polymerization steps, the kinetics are likely to be greatly enhanced at
555 higher concentrations of the organic reactants. One possibility for enhanced concentration of

556 organic reactants is the potential preference of the reactants for the aerosol surface. If polyacetals
557 partition to the aerosol surface as they do in our bulk experiments, their further polymerization
558 with each other and with condensing organics would be enhanced; polymerization could be
559 similarly enhanced if carbonyl and/or alcohol reactants partition to the aerosol surface or to
560 organic inclusions. This possibility is supported by the recent work of Li et al. (2011), Schwier et
561 al. (2010) and Sareen et al. (2010) demonstrating surface tension depression by surface-active
562 species formed in solutions of formaldehyde, acetaldehyde, glyoxal and/or methylglyoxal in pure
563 water and/or aqueous ammonium sulfate. Additionally, products of cross-reactions between
564 methylglyoxal and formaldehyde or acetaldehyde had a larger effect on surface tension than
565 could be explained by self-reactions alone.

566 An additional possibility for enhanced concentrations of organic reactants favorable for
567 polyacetal formation is transport of organic-rich aerosols from the lower troposphere to the
568 UT/LS. Polyacetal formation could be initiated on such aerosols upon condensation of H_2SO_4
569 and/or coagulation with H_2SO_4 particles formed near the tropopause. In order to evaluate the
570 likelihood of this process, carbonyl species more typical of photochemically aged tropospheric
571 aerosols (less volatile and likely more oxidized than propanal) should be evaluated for their
572 potential to participate in acid-catalyzed polyacetal formation.

573 In addition to the major species identified in the films, aldol condensation products of higher
574 order than the dimer, 2-methyl-2-pentenal, must also be present as minor species in order to
575 account for the strong absorbance of visible light by the films. The absorbing species in the films
576 most likely form in the solutions and then partition to the organic film since both the films and
577 the solutions they form on are highly colored. If light-absorbing aldol condensation products in
578 aerosols undergo similar partitioning into organic coatings, it would increase their potential
579 impact on the optical properties of aerosols.

580

581 **5 Conclusions**

582 In summary, bulk solutions of propanal and sulfuric acid at UT/LS aerosol acidities produced
583 surface films that absorbed strongly in the visible and that were composed primarily of aldol
584 condensation products and polyacetals. When glyoxal and/or methylglyoxal were also present in
585 solution, acetal products of cross-reactions were observed in the films while the presence of
586 glyoxal also significantly increased the rate of film formation. Both of these results suggest that

587 polyacetal reaction products such as those found in the films may be important when the variety
588 of atmospheric gas and aerosol phase organic species available to serve as reactants is
589 considered. Even if polyacetals and light-absorbing aldol condensation products do not account
590 for a significant fraction of aerosol organic mass, their impact on aerosol radiative and CCN
591 properties could be significant if they partition to the aerosol surface.

592

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606

607

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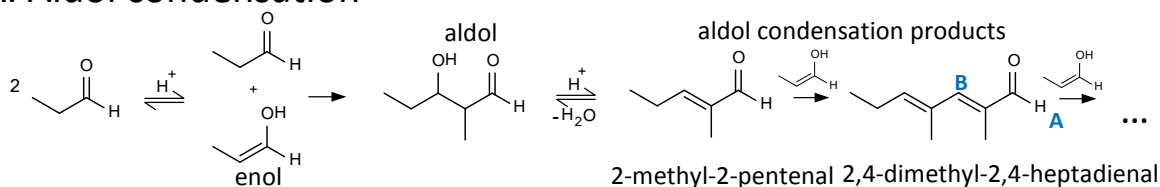
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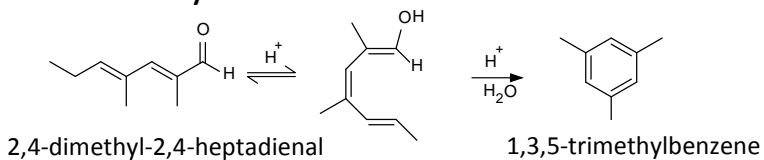
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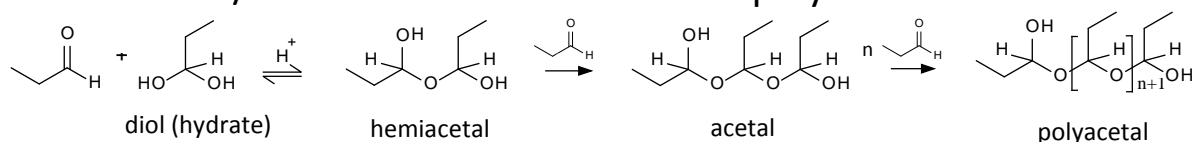
A. Aldol condensation



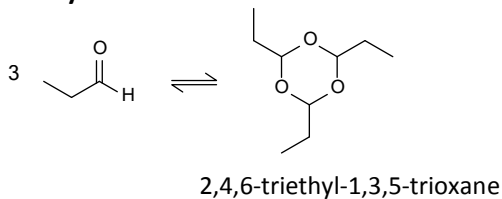
B. Trimethylbenzene formation



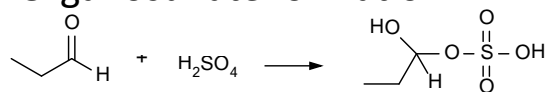
C. Hemiacetal/acetal formation and further polymerization



D. Cyclotrimerization



E. Organosulfate formation

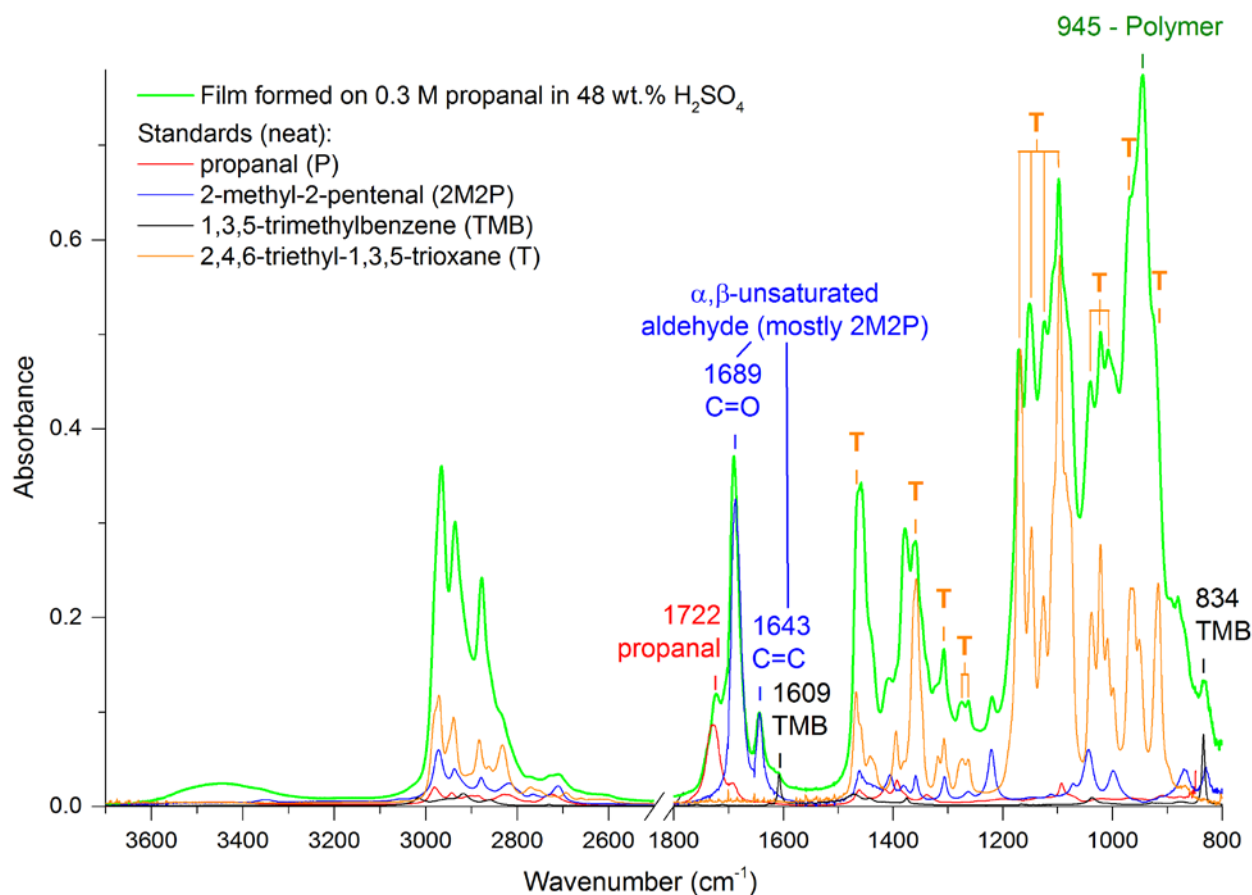


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868 Figure 1. Potential reactions of propanal in the presence of sulfuric acid. Selected hydrogen

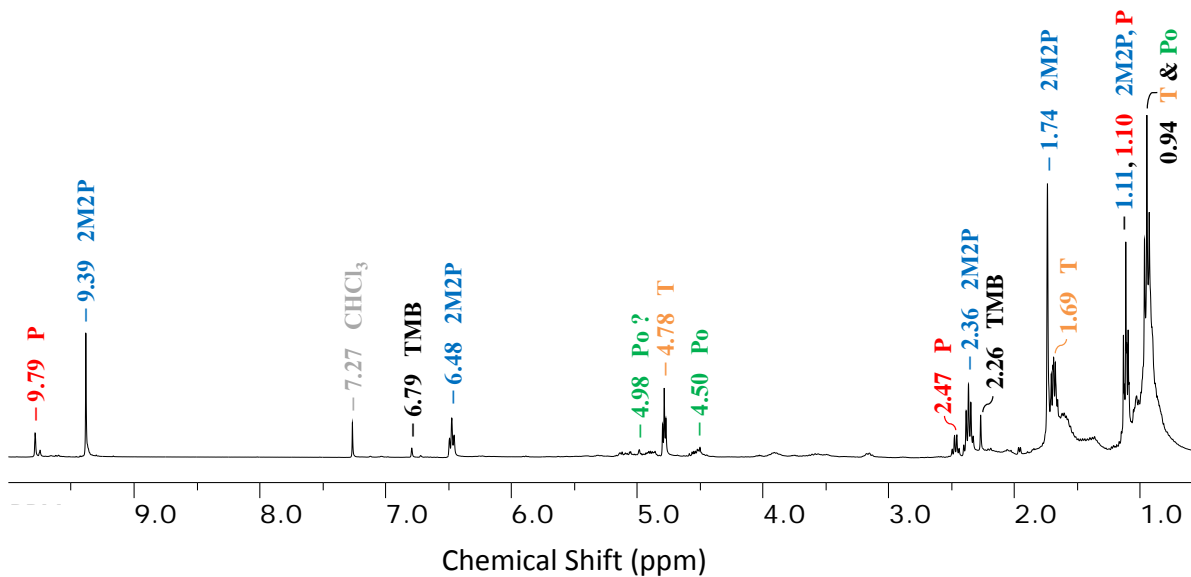
869 positions are labelled A and B in blue to facilitate discussion in the text.



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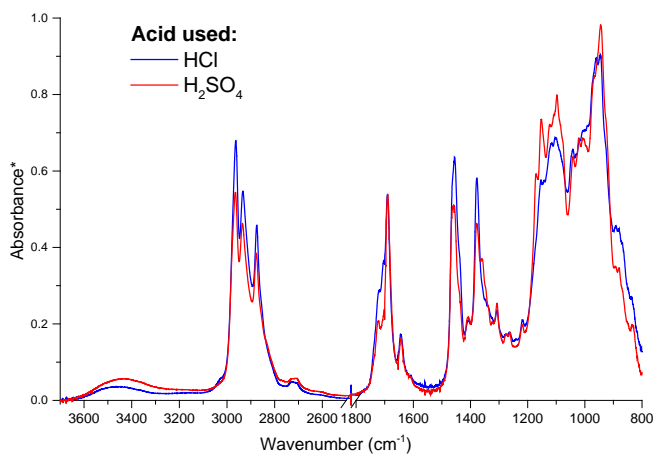
872 Figure 2. Typical ATR-FTIR spectrum of a surface film formed on 0.30 M propanal in 48 wt %
 873 H₂SO₄ (7 days after mixing) compared to neat standards. Spectra of standards for propanal, 2-
 874 methyl-2-pentenal, 1,3,5-trimethylbenzene and 2,4,6-triethyl-1,3,5-trioxane are scaled to indicate
 875 their maximum possible contribution to the film spectrum. The positions of the major trioxane
 876 peaks are indicated with the abbreviation **T** to illustrate their presence in the spectrum of the
 877 film. Other important peaks are labelled with wavenumber and their assignments as discussed in
 878 the text. Note that the region from 2500-1800 cm⁻¹ lacks peaks and is omitted for clarity. For
 879 details of the lower-intensity traces, see Figure S2 in the Supplement which provides a version of
 880 this figure covering the smaller absorbance range of 0 – 0.15.



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882

883 Figure 3. ^1H NMR spectrum of a surface film formed on 0.30 M propanal in 48 wt % H_2SO_4 (7
 884 days after mixing). The film was dissolved in CDCl_3 . The ATR-FTIR spectrum for this same
 885 film is shown in Fig. 2. All major peaks have been assigned to the following five dominant
 886 species: P = propanal, 2M2P = 2-methyl-2-pental, TMB = 1,3,5-trimethybenzene, Po =
 887 polymer, T = 2,4,6-triethyl-1,3,5-trioxane.



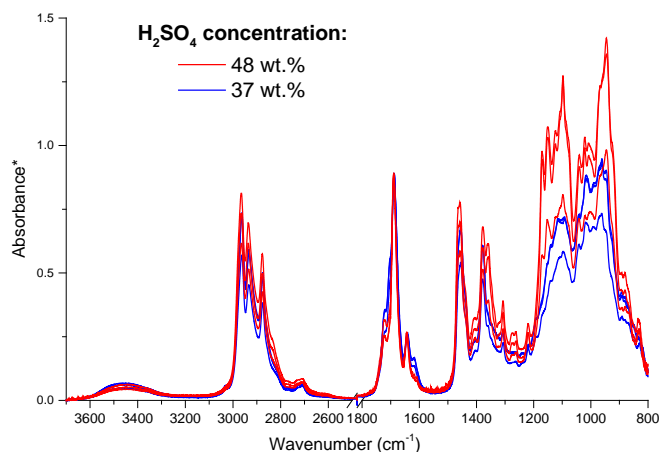
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890 Figure 4. ATR-FTIR spectra of films formed on 0.30 M propanal at pH = -0.85 in H₂SO₄ (48 wt
891 %) and in HCl (7 days after mixing). The region from 2500-1800 cm⁻¹ is omitted for clarity.

892 *Absorbance spectra are scaled to the C=O peak at 1690 cm⁻¹ from aldol condensation products

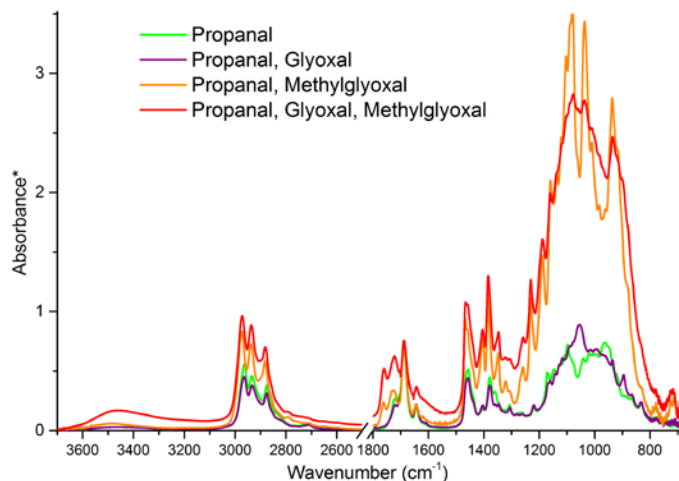
893 (predominantly 2-methyl-2-pentenal).



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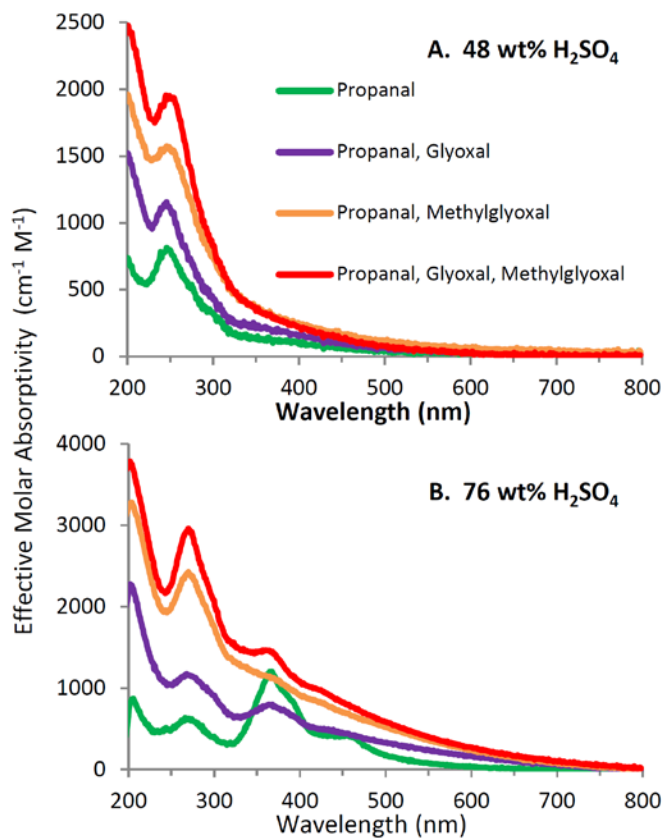
896 Figure 5. Effect of acidity on the ATR-FTIR spectra of surface films formed on 0.30 M propanal
897 in H₂SO₄ (7 days after mixing). Triplicates are shown for both 48 and 37 wt % H₂SO₄. The
898 region from 2500-1800 cm⁻¹ is omitted for clarity. *Absorbance spectra are scaled to the C=O
899 peak at 1690 cm⁻¹ from aldol condensation products (predominantly 2-methyl-2-pentenal) in
900 order to illustrate differences between relative peak intensities.



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902

903 Figure 6: ATR-FTIR spectra of surface films formed on mixtures of propanal with glyoxal
 904 and/or methylglyoxal in 48 wt % H₂SO₄ (7 days after mixing). Solutions are 0.30 M in each
 905 organic. The region from 2500-1800 cm⁻¹ is omitted for clarity. *Absorbance spectra are scaled
 906 to the C=O peak at 1690 cm⁻¹ from aldol condensation products (predominantly 2-methyl-2-
 907 pentenal) in order to illustrate differences between relative peak intensities. Spectra of replicates
 908 are provided in the Supplement (Figs. S3 and S4).



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911 Figure 7. UV-visible absorption spectra of aged film-forming solutions. Solutions are 0.030 M in
 912 each organic and were prepared in A. 48 wt % H_2SO_4 or B. 76 wt % H_2SO_4 and stored for 274
 913 days. “Effective” molar absorptivity is calculated based only on the concentration of the propanal
 914 reactant (0.030 M) so that any changes in absorbance (compared to the propanal-only spectrum)
 915 must be due to the presence of the additional organic species.