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

A. L. Van Wyngarden[1], S. Pérez-Montaño[1], J. V. H. Bui[1], E. S. W. Li[1], T. E. Nelson[1], K. T. Ha[1], L. Leong[1], L. T. Iraci[2]

[1] Department of Chemistry, San José State University, San José, CA 95192, USA

[2] Atmospheric Science Branch, NASA Ames Research Center, Moffett Field, CA 94035, USA

Correspondence to: A. L. Van Wyngarden (Annalise.VanWyngarden@sjsu.edu)

Abstract

Particles in the upper troposphere and lower stratosphere (UT/LS) consist mostly of concentrated sulfuric acid (40-80 wt %) in water. However, airborne measurements have shown that these particles also contain a significant fraction of organic compounds of unknown chemical composition. Acid-catalyzed reactions of carbonyl species are believed to be responsible for significant transfer of gas phase organic species into tropospheric aerosols and are potentially more important at the high acidities characteristic of UT/LS particles. In this study, experiments combining sulfuric acid (H_2SO_4) with propanal and with mixtures of propanal with glyoxal and/or methylglyoxal at acidities typical of UT/LS aerosols produced highly colored surface films (and solutions) that may have implications for aerosol properties. In order to identify the chemical processes responsible for the formation of the surface films, Attenuated Total Reflectance – Fourier Transform Infrared and [1]H Nuclear Magnetic Resonance spectroscopies were used to analyze the chemical composition of the films. Films formed from propanal were a complex mixture of aldol condensation products, acetals and propanal itself. The major aldol condensation products were the dimer (2-methyl-2-pentenal) and 1,3,5-trimethylbenzene, which was formed by cyclization of the linear aldol condensation trimer. Additionally, the strong visible absorption of the films indicates that higher order aldol condensation products must also be present as minor species. The major acetal species were 2,4,6-triethyl-1,3,5-trioxane and longer-chain linear polyacetals which are likely to separate from the aqueous phase. Films formed on mixtures of propanal with glyoxal and/or methylglyoxal also showed evidence for

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

1   Introduction

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

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

3

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 [1]H Nuclear Magnetic Resonance (^{1}H 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 (H_2SO_4). 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 ^{1}H 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 % H_2SO_4)

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   H_2SO_4. Specifically, films were first observed on propanal-only samples after 4 days in 48 wt %

229   H_2SO_4, versus 5-10 days in 76 wt % H_2SO_4; and visible film formation on

230   propanal/methylglyoxal and propanal/glyoxal/methylglyoxal samples required 5-22 days in 48

231   wt % H_2SO_4, while samples in 76 wt % H_2SO_4 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 ^{1}H 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 2.27 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

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 ^{1}H 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 CH$_2$ and CH$_3$ 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

3.2.3 Other potential film components: organosulfates, etc.

In order to test for the presence of organosulfates, reaction mixtures were prepared with hydrochloric acid at the same pH as the sulfuric acid mixtures. The formation of surface films on these mixtures demonstrates that organosulfates are not necessary for film formation, and the similarity of the ATR-FTIR spectra for films formed on sulfuric acid and hydrochloric acid solutions (example shown in Fig. 4 for 0.30 M propanal/48 wt % H_2SO_4) demonstrates that organosulfates are not present in significant quantities. We note, however, that organosulfates could still be produced in the sulfuric acid solutions, where they would be expected to remain due to their ionizability.

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

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

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 ~0.94ppm).

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

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 C=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

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

The FTIR spectrum of the film from propanal and methlyglyoxal deviates even farther from that of propanal-only. Not only does it lack the signature of 2,4,6-triethyl-1,3,5-trioxane, indicating products of cross-reactions, but, additionally, absorbance in the entire 1500-900 cm^{-1} region is much stronger relative to the aldol condensation peak at 1690 cm^{-1}, indicating a stronger relative contribution from acetal species. 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.

3.6   UV-vis spectra of solutions

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

16

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 ~ 9 cm^{-1} 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.

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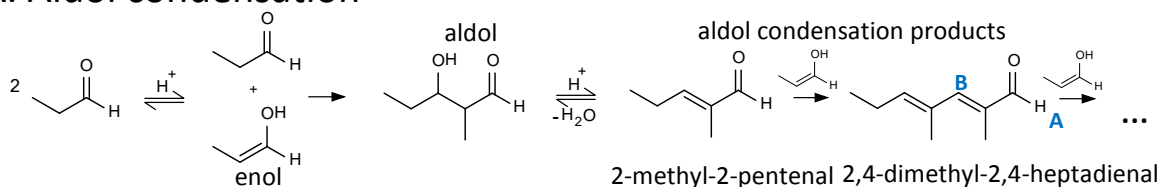
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865

A. Aldol condensation

aldol

aldol condensation products

enol

2-methyl-2-pentenal   2,4-dimethyl-2,4-heptadienal

B. Trimethylbenzene formation

2,4-dimethyl-2,4-heptadienal   1,3,5-trimethylbenzene
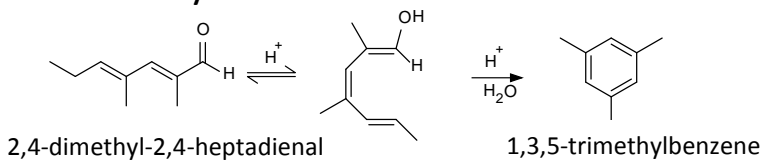
C. Hemiacetal/acetal formation and further polymerization

diol (hydrate)   hemiacetal   acetal   polyacetal

D. Cyclotrimerization

2,4,6-triethyl-1,3,5-trioxane
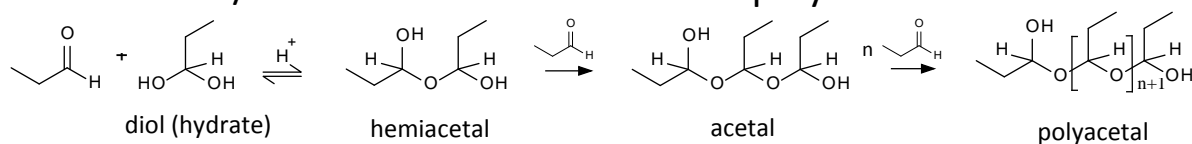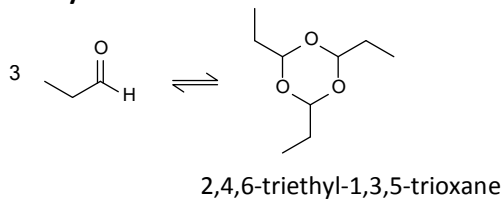
E. Organosulfate formation
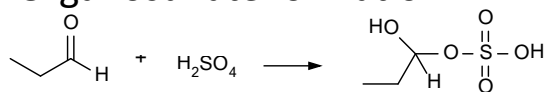
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868   Figure 1. Potential reactions of propanal in the presence of sulfuric acid. Selected hydrogen

869   positions are labelled A and B in blue to facilitate discussion in the text.
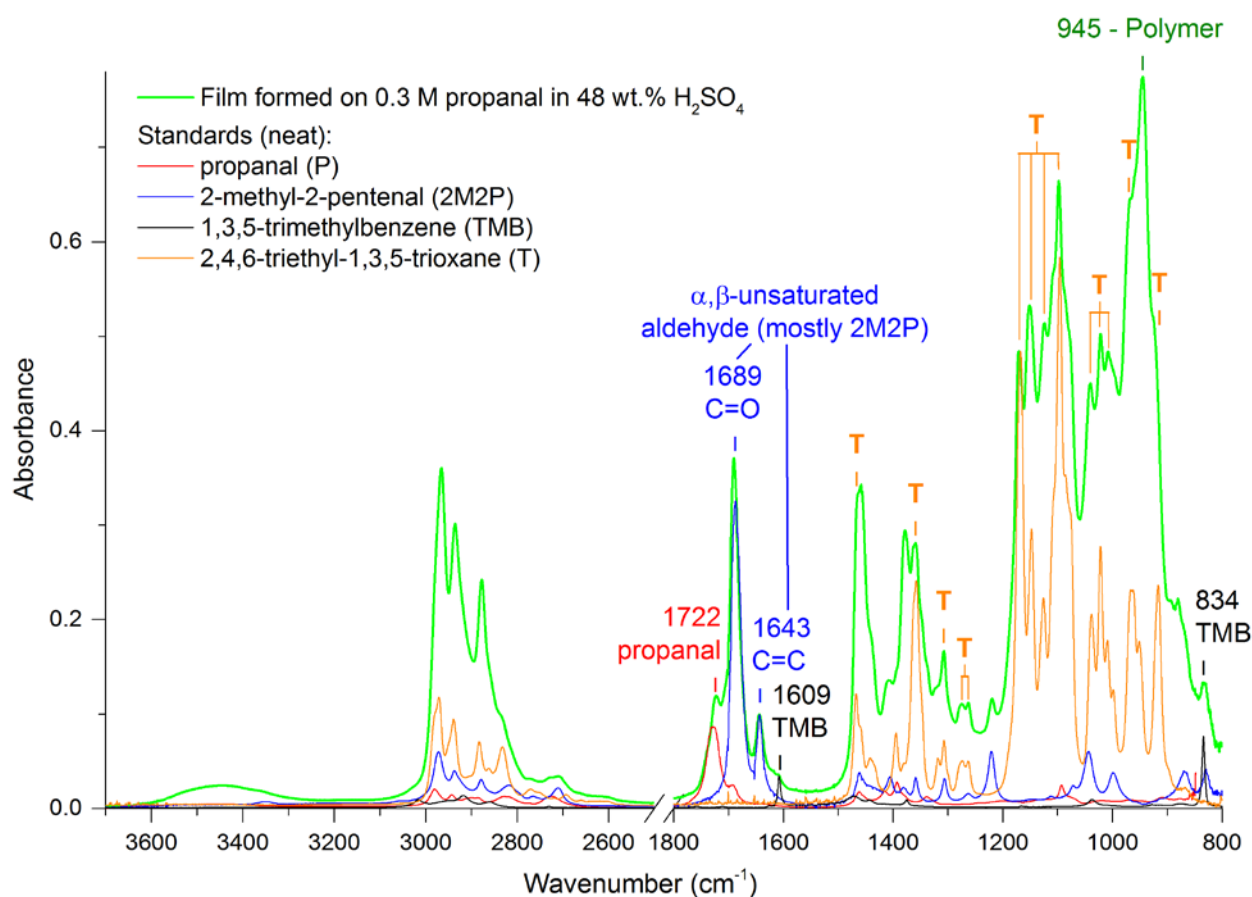
Figure 2. Typical ATR-FTIR spectrum of a surface film formed on 0.30 M propanal in 48 wt % H_2SO_4 (7 days after mixing) compared to neat standards. Spectra of standards for propanal, 2-methyl-2-pentenal, 1,3,5-trimethylbenzene and 2,4,6-triethyl-1,3,5-trioxane are scaled to indicate their maximum possible 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. Other important peaks are labelled with wavenumber and their assignments as discussed in the text. Note that the region from 2500-1800 cm^{-1} lacks peaks and is omitted for clarity. For details of the lower-intensity traces, see Figure S2 in the Supplement which provides a version of this figure covering the smaller absorbance range of 0 – 0.15.

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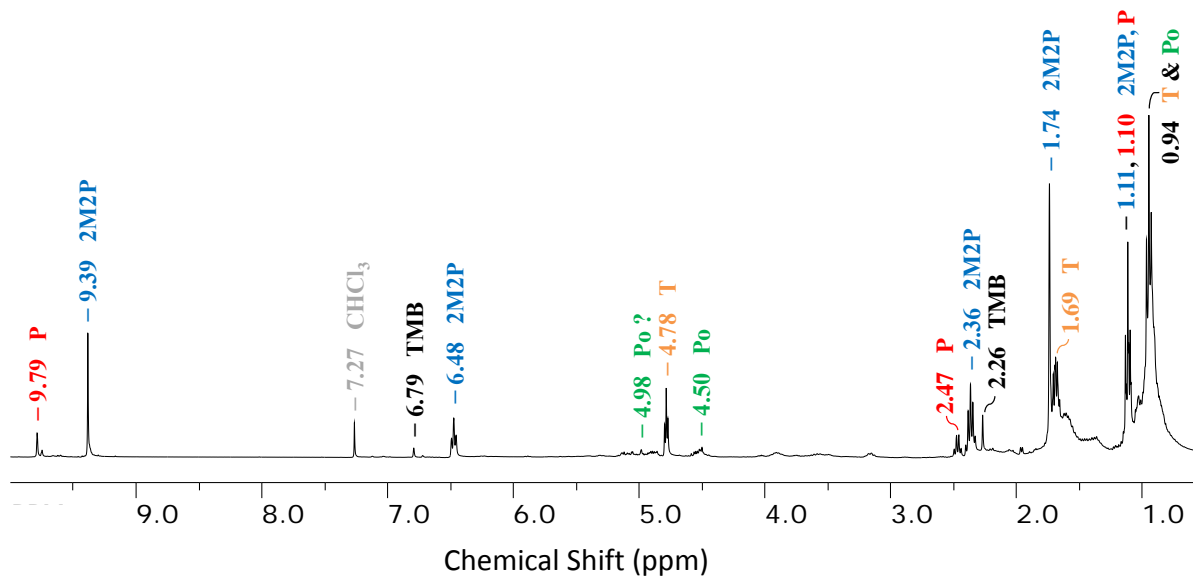
Figure 3. ^{1}H NMR spectrum of a surface film formed on 0.30 M propanal in 48 wt % H_2SO_4 (7 days after mixing). The film was dissolved in $CDCl_3$. The ATR-FTIR spectrum for this same film is shown in Fig. 2. All major peaks have been assigned to the following five dominant species: P = propanal, 2M2P = 2-methyl-2-pentenal, TMB = 1,3,5-trimethybenzene, Po = polymer, T = 2,4,6-triethyl-1,3,5-trioxane.
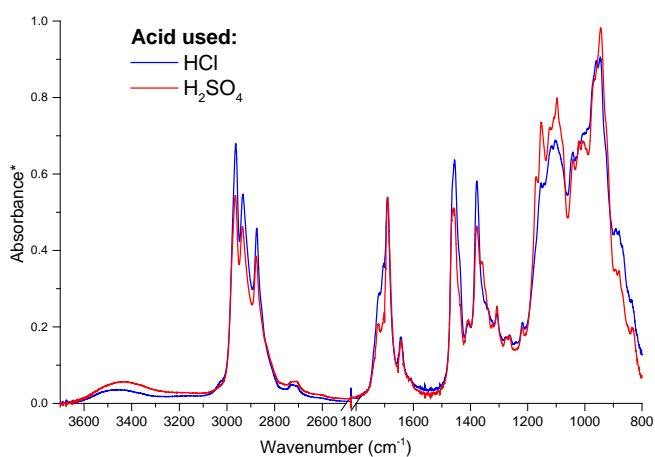
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890 Figure 4. ATR-FTIR spectra of films formed on 0.30 M propanal at pH = -0.85 in H_2SO_4 (48 wt

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

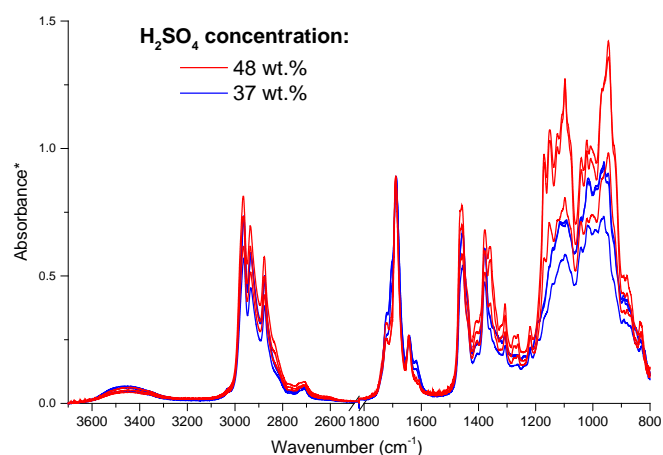893 (predominantly 2-methyl-2-pentenal).

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895

896 Figure 5. Effect of acidity on the ATR-FTIR spectra of surface films formed on 0.30 M propanal

897 in H_2SO_4 (7 days after mixing). Triplicates are shown for both 48 and 37 wt % H_2SO_4. 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

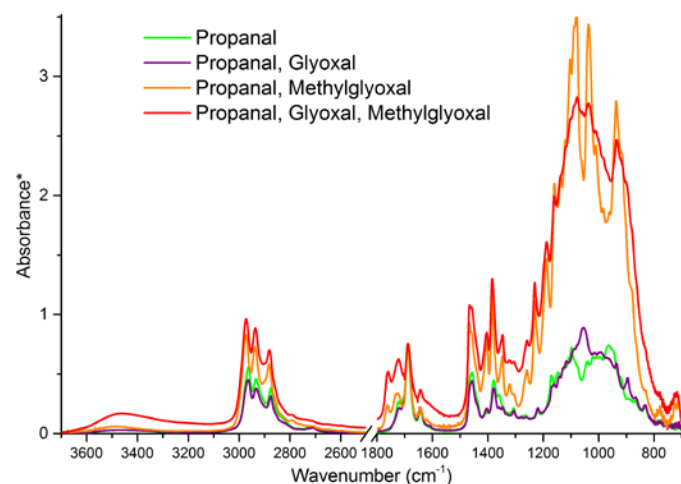900 order to illustrate differences between relative peak intensities.

Figure 6: ATR-FTIR spectra of surface films formed on mixtures of propanal with glyoxal and/or methylglyoxal in 48 wt % H_2SO_4 (7 days after mixing). Solutions are 0.30 M in each organic. The region from 2500-1800 cm^{-1} is omitted for clarity. *Absorbance spectra are scaled to the C=O peak at 1690 cm^{-1} from aldol condensation products (predominantly 2-methyl-2-pentenal) in order to illustrate differences between relative peak intensities. Spectra of replicates are provided in the Supplement (Figs. S3 and S4).
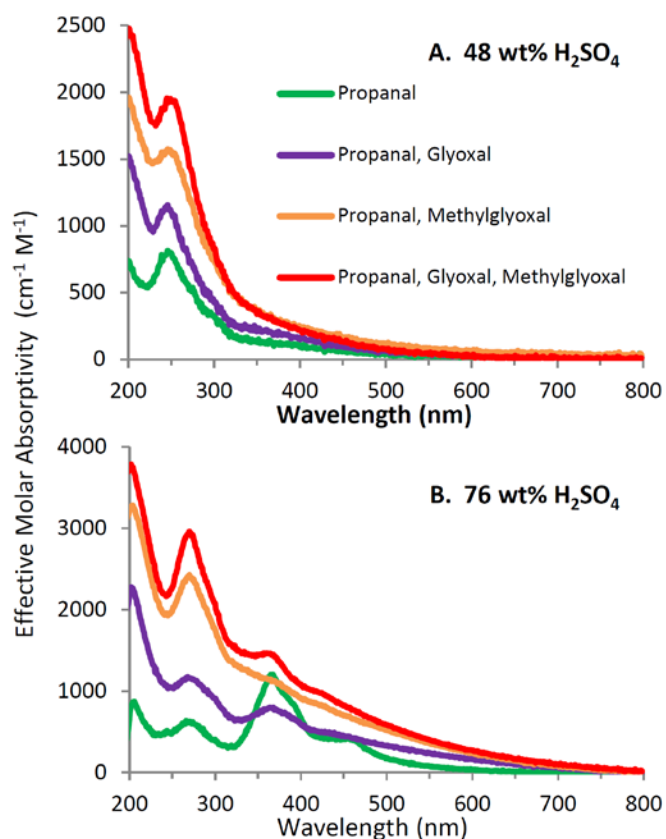
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Figure 7. UV-visible absorption spectra of aged film-forming solutions. Solutions are 0.030 M in each organic and were prepared in A. 48 wt % H_2SO_4 or B. 76 wt % H_2SO_4 and stored for 274 days. "Effective" molar absorptivity is calculated based only on the concentration of the propanal reactant (0.030 M) so that any changes in absorbance (compared to the propanal-only spectrum) must be due to the presence of the additional organic species.