2017 Astrobiology Graduate Conference

Charlottesville, VA

1
00:00:00,790 --> 00:00:07,509
[Music]

2
00:00:12,080 --> 00:00:10,120
so I'm going to be continuing the lipid

3
00:00:13,879 --> 00:00:12,090
discussion a little bit although I'm

4
00:00:15,829 --> 00:00:13,889
going to take a bit of a step back and

5
00:00:17,990 --> 00:00:15,839
talk about how we can make potential

6
00:00:19,189 --> 00:00:18,000
lipids I think maybe what we're learning

7
00:00:21,099 --> 00:00:19,199
most of all is that we're not

8
00:00:24,109 --> 00:00:21,109
particularly creative picking wikimedia

9
00:00:25,340 --> 00:00:24,119
slides but the great news is i can skip

10
00:00:27,050 --> 00:00:25,350
all of my intro and focus on the

11
00:00:31,160 --> 00:00:27,060
detailed or mechanistic organic

12
00:00:32,959 --> 00:00:31,170
chemistry um I won't do that um anyway

13
00:00:36,500 --> 00:00:32,969

so lipids are important membranes are

14
00:00:38,869 --> 00:00:36,510
important when I'm talking about lipids

15
00:00:41,330 --> 00:00:38,879
and surfactants we already had a really

16
00:00:43,850 --> 00:00:41,340
good explanation of this but I tend to

17
00:00:46,910 --> 00:00:43,860
think about polar head groups and

18
00:00:48,319 --> 00:00:46,920
nonpolar fatty tails which will

19
00:00:50,389 --> 00:00:48,329
partition preferentially to the air

20
00:00:51,920 --> 00:00:50,399
water interface and will also form

21
00:00:55,760 --> 00:00:51,930
through dimensional structures as we've

22
00:00:57,049 --> 00:00:55,770
just seen this has a lot of the same

23
00:00:59,240 --> 00:00:57,059
information that we just thought but

24
00:01:01,580 --> 00:00:59,250
essentially you've got your simple fatty

25
00:01:04,609 --> 00:01:01,590
acids that are used as your prebiotic

26
00:01:07,880 --> 00:01:04,619
irrelevant model systems and then you

27
00:01:09,859 --> 00:01:07,890
can also make vesicles out of

28
00:01:12,740 --> 00:01:09,869
phospholipids which are much more

29
00:01:14,990 --> 00:01:12,750
complex but not particularly prebiotic

30
00:01:16,670 --> 00:01:15,000
irrelevant a few other things about the

31
00:01:19,520 --> 00:01:16,680
vesicles that these two systems make

32
00:01:21,859 --> 00:01:19,530
fatty acids make vesicles but they tend

33
00:01:24,530 --> 00:01:21,869
to be very pH and salt dependent and

34
00:01:26,149 --> 00:01:24,540
very sort of conditionally dependent and

35
00:01:28,460 --> 00:01:26,159
also tend to be a little bit leaky ER

36
00:01:30,800 --> 00:01:28,470
than phospholipids do whereas

37
00:01:32,690 --> 00:01:30,810
phospholipid best vesicles form at much

38
00:01:35,719 --> 00:01:32,700

lower concentrations and are stable

39
00:01:37,670 --> 00:01:35,729
under many sort of a much wider range of

40
00:01:39,590 --> 00:01:37,680
conditions but in the absence of the

41
00:01:42,050 --> 00:01:39,600
inclusions and things that modern life

42
00:01:44,420 --> 00:01:42,060
has they tend to not allow a lot they

43
00:01:45,859 --> 00:01:44,430
tend to be very impermeable so one of

44
00:01:48,350 --> 00:01:45,869
the things that we're thinking about is

45
00:01:50,420 --> 00:01:48,360
what if we had something that sort of

46
00:01:52,190 --> 00:01:50,430
explored the chemical space in between

47
00:01:54,050 --> 00:01:52,200
these two things so you can think about

48
00:01:56,690 --> 00:01:54,060
phospholipids being robust but not very

49
00:01:58,639 --> 00:01:56,700
permeable fatty acid vesicles being

50
00:02:00,800 --> 00:01:58,649
permeable but not very robust but

51
00:02:02,420 --> 00:02:00,810
there's sort of this wide range of other

52
00:02:05,749 --> 00:02:02,430
possibilities that we're looking to

53
00:02:07,130 --> 00:02:05,759
explore and in particular obviously we

54
00:02:09,499 --> 00:02:07,140
know that the head group of the

55
00:02:11,270 --> 00:02:09,509
phospholipids is very important but also

56
00:02:12,680 --> 00:02:11,280
the fact that you can have single tailed

57
00:02:13,460 --> 00:02:12,690
or double tailed lipids is also

58
00:02:15,050 --> 00:02:13,470
important so we're

59
00:02:16,730 --> 00:02:15,060
sort of looking for ways of making

60
00:02:18,560 --> 00:02:16,740
double tailed lipids and that's where

61
00:02:21,100 --> 00:02:18,570
prebiotic chemical synthesis comes into

62
00:02:25,550 --> 00:02:21,110
play and looking at a simple abiotic

63
00:02:26,600 --> 00:02:25,560

synthesis of multi tailed lipids so when

64
00:02:28,340 --> 00:02:26,610
we're thinking about this we have to

65
00:02:30,110 --> 00:02:28,350
pick environmental conditions and as

66
00:02:31,930 --> 00:02:30,120
many people in this room know our lab

67
00:02:34,460 --> 00:02:31,940
tends to like to use sunlight and water

68
00:02:37,430 --> 00:02:34,470
and so the Sun is a really good energy

69
00:02:40,040 --> 00:02:37,440
source because it is the largest energy

70
00:02:42,710 --> 00:02:40,050
source even on a prebiotic earth with

71
00:02:44,540 --> 00:02:42,720
the faint young Sun and all of that it's

72
00:02:47,840 --> 00:02:44,550
also a low entropy source so you know

73
00:02:50,990 --> 00:02:47,850
you're not giving off a lot of it tends

74
00:02:53,210 --> 00:02:51,000
to be very specific and then in terms of

75
00:02:54,920 --> 00:02:53,220
environments we like water and air water

76
00:02:56,210 --> 00:02:54,930
interfaces in particular because they

77
00:02:58,670 --> 00:02:56,220
would have been widely available and

78
00:03:01,340 --> 00:02:58,680
relatively gentle um so just to talk a

79
00:03:03,650 --> 00:03:01,350
little bit about the young Sun many

80
00:03:05,420 --> 00:03:03,660
people know that when we're talking in

81
00:03:08,360 --> 00:03:05,430
the period of sort of prebiotic chemical

82
00:03:11,180 --> 00:03:08,370
evolution when we're talking the Sun was

83
00:03:14,960 --> 00:03:11,190
quite a bit less luminous about 25% less

84
00:03:19,130 --> 00:03:14,970
luminous than it is today but there was

85
00:03:21,710 --> 00:03:19,140
still plenty of the UV radiation that is

86
00:03:25,370 --> 00:03:21,720
sort of high-energy and useful UV

87
00:03:27,170 --> 00:03:25,380
radiation and more of that high-energy

88
00:03:28,340 --> 00:03:27,180

UV radiation so not the super

89
00:03:30,699 --> 00:03:28,350
high-energy stuff we were talking about

90
00:03:34,009 --> 00:03:30,709
before but the sort of nice near UV

91
00:03:35,780 --> 00:03:34,019
energy more of that would have reached

92
00:03:37,220 --> 00:03:35,790
the surface of earth because we didn't

93
00:03:39,590 --> 00:03:37,230
have oxygen and because we didn't have

94
00:03:42,080 --> 00:03:39,600
the ozone layer shielding it and so

95
00:03:44,030 --> 00:03:42,090
we've heard a lot about how that UV

96
00:03:48,100 --> 00:03:44,040
radiation can destroy things but my

97
00:03:51,500 --> 00:03:48,110
point is it can also build things up um

98
00:03:53,210 --> 00:03:51,510
yeah okay and besides the fact that the

99
00:03:55,729 --> 00:03:53,220
Sun was the largest energy source

100
00:03:57,410 --> 00:03:55,739
available photochemistry is also

101
00:03:59,150 --> 00:03:57,420
fundamentally different from thermal

102
00:04:01,009 --> 00:03:59,160
chemistry thermal chemistry you can

103
00:04:03,170 --> 00:04:01,019
think about just shaking molecules and

104
00:04:06,050 --> 00:04:03,180
cooking them to a point where they react

105
00:04:08,180 --> 00:04:06,060
whereas with photochemistry it's very

106
00:04:09,920 --> 00:04:08,190
molecule specific and you can excite one

107
00:04:11,990 --> 00:04:09,930
molecule and the molecule next to it can

108
00:04:14,060 --> 00:04:12,000
be very can be completely unaffected so

109
00:04:16,460 --> 00:04:14,070
you don't have to heat stuff up and you

110
00:04:19,039 --> 00:04:16,470
can get much sort of more high energy

111
00:04:21,199 --> 00:04:19,049
and out of equilibrium reactions to

112
00:04:25,310 --> 00:04:21,209
occur than you would get with thermal

113
00:04:27,120 --> 00:04:25,320

chemistry um and it's also molecule

114
00:04:29,100 --> 00:04:27,130
specific so you can start with three ml

115
00:04:32,130 --> 00:04:29,110
fuels that look very similar so you have

116
00:04:34,920 --> 00:04:32,140
hexanol hexanoic acid and tuoc so

117
00:04:36,870 --> 00:04:34,930
hexanoic acid and you can see that only

118
00:04:39,510 --> 00:04:36,880
the two oXXO hexanoic acid with the

119
00:04:44,250 --> 00:04:39,520
extra carbonyl is absorbing light in the

120
00:04:47,010 --> 00:04:44,260
near UV region and so it's very molecule

121
00:04:49,500 --> 00:04:47,020
specific it's also incredibly

122
00:04:51,510 --> 00:04:49,510
environment specific so these molecules

123
00:04:54,330 --> 00:04:51,520
so pyruvic acid which may be more

124
00:04:58,230 --> 00:04:54,340
familiar to biologists as pyruvate when

125
00:05:00,960 --> 00:04:58,240
it's deprotonated is in the gas phase

126
00:05:02,490 --> 00:05:00,970
absorbs light about 350 nanometers but

127
00:05:06,360 --> 00:05:02,500
as soon as you put it in water it blue

128
00:05:07,920 --> 00:05:06,370
shifts slightly and absorbs at about 320

129
00:05:09,990 --> 00:05:07,930
nanometers instead so there's a shift

130
00:05:12,090 --> 00:05:10,000
that occurs but you'll notice that as we

131
00:05:14,100 --> 00:05:12,100
add an alkyl tail there really isn't

132
00:05:16,200 --> 00:05:14,110
much shift in the absorption

133
00:05:18,000 --> 00:05:16,210
cross-section and so it's very much more

134
00:05:22,200 --> 00:05:18,010
dependent on the functional group than

135
00:05:23,400 --> 00:05:22,210
it is on the alkyl tail and the

136
00:05:26,370 --> 00:05:23,410
photochemistry

137
00:05:28,110 --> 00:05:26,380
that these molecules follow the

138
00:05:30,270 --> 00:05:28,120

mechanism is completely different in the

139
00:05:32,010 --> 00:05:30,280
aqueous phase than in the gas phase and

140
00:05:33,410 --> 00:05:32,020
i'm happy to talk all of the details

141
00:05:36,600 --> 00:05:33,420
about not going to stick photo chemistry

142
00:05:39,180 --> 00:05:36,610
if you want but i'm only going to go

143
00:05:41,040 --> 00:05:39,190
into some of it and so what we've been

144
00:05:43,470 --> 00:05:41,050
doing over the last few years is going

145
00:05:46,310 --> 00:05:43,480
through a whole set of these alpha keto

146
00:05:48,720 --> 00:05:46,320
acids or oxoacids as I will call them

147
00:05:50,310 --> 00:05:48,730
starting with the shortest which is

148
00:05:53,490 --> 00:05:50,320
pyruvic acid which just has this little

149
00:05:56,220 --> 00:05:53,500
methyl tail and then a series of other

150
00:05:58,890 --> 00:05:56,230
molecules going up to the 12 carbon to

151
00:06:00,900 --> 00:05:58,900
oxygen ohmic acid I'll be talking mostly

152
00:06:02,300 --> 00:06:00,910
about 2ak so after Noack acid just

153
00:06:04,440 --> 00:06:02,310
because you can purchase it from sigma

154
00:06:07,170 --> 00:06:04,450
and it doesn't have to be custom

155
00:06:09,630 --> 00:06:07,180
synthesized and so we have a very simple

156
00:06:11,600 --> 00:06:09,640
photochemical reactor we use a xenon arc

157
00:06:15,600 --> 00:06:11,610
lamp which is a good solar simulator and

158
00:06:18,000 --> 00:06:15,610
we just shine light on a solution of our

159
00:06:21,090 --> 00:06:18,010
molecule in water we can control the

160
00:06:23,610 --> 00:06:21,100
atmosphere the gas composition of the

161
00:06:29,010 --> 00:06:23,620
reactor as well but it's a very simple

162
00:06:30,930 --> 00:06:29,020
setup um but I like a simpler picture of

163
00:06:32,670 --> 00:06:30,940

what's going on so you have and here I'm

164
00:06:35,430 --> 00:06:32,680
just showing pyruvic acid because it's

165
00:06:37,740 --> 00:06:35,440
the easiest one and so you've got

166
00:06:39,930 --> 00:06:37,750
pyruvic acid floating around in your

167
00:06:40,260 --> 00:06:39,940
solution but one of the things to keep

168
00:06:42,780 --> 00:06:40,270
in my

169
00:06:44,880 --> 00:06:42,790
mind is that pyruvic acid isn't just

170
00:06:46,980 --> 00:06:44,890
pyruvic acid in solution you also get

171
00:06:47,400 --> 00:06:46,990
hydration reactions to form the geminal

172
00:06:51,900 --> 00:06:47,410
diol

173
00:06:53,850 --> 00:06:51,910
light because you've removed the

174
00:06:54,900 --> 00:06:53,860
carbonyl chromophore so you have to keep

175
00:06:56,580 --> 00:06:54,910
in mind that there's an equilibrium

176
00:06:59,100 --> 00:06:56,590
between the two of these and it's

177
00:07:01,470 --> 00:06:59,110
dependent on the pH and the

178
00:07:05,640 --> 00:07:01,480
concentration of the molecules in

179
00:07:08,190 --> 00:07:05,650
solution what the exact ratio is but you

180
00:07:10,580 --> 00:07:08,200
still unlike many die carbonyls you

181
00:07:13,320 --> 00:07:10,590
still retain a lot of your absorptive

182
00:07:15,660 --> 00:07:13,330
feature and so you can still do lots of

183
00:07:17,610 --> 00:07:15,670
photo chemistry with your Axio acids

184
00:07:21,780 --> 00:07:17,620
where you wouldn't with an aldehyde or a

185
00:07:22,950 --> 00:07:21,790
ketone and so your simple picture looks

186
00:07:25,410 --> 00:07:22,960
a little bit more like you've got

187
00:07:28,050 --> 00:07:25,420
pyruvic acid and then the dial floating

188
00:07:30,750 --> 00:07:28,060

around in solution but if we hit that

189
00:07:34,530 --> 00:07:30,760
with sunlight we can excite these

190
00:07:36,840 --> 00:07:34,540
molecules and the excited state so you

191
00:07:38,760 --> 00:07:36,850
excite to the singlet you undergo inter

192
00:07:40,350 --> 00:07:38,770
system crossing and internal conversion

193
00:07:43,770 --> 00:07:40,360
to the triplet state for those of you

194
00:07:45,780 --> 00:07:43,780
who care and then those molecules can

195
00:07:47,160 --> 00:07:45,790
react the excited molecule can react

196
00:07:49,860 --> 00:07:47,170
with the other molecules that are

197
00:07:52,110 --> 00:07:49,870
floating around in solution and so you

198
00:07:53,940 --> 00:07:52,120
can undergo a process called hydrogen

199
00:07:56,700 --> 00:07:53,950
abstraction and you can do this from

200
00:07:59,640 --> 00:07:56,710
either the dial form or the carbonyl

201
00:08:02,190 --> 00:07:59,650
form and essentially what you're doing

202
00:08:04,530 --> 00:08:02,200
is you're making organic radicals in

203
00:08:06,150 --> 00:08:04,540
solution and there's a series of

204
00:08:07,740 --> 00:08:06,160
different radicals you can make you can

205
00:08:09,840 --> 00:08:07,750
hydrogen abstract from the carboxyl

206
00:08:11,760 --> 00:08:09,850
group or you can hydrogen abstract from

207
00:08:15,480 --> 00:08:11,770
this methyl group which is something

208
00:08:18,300 --> 00:08:15,490
we've just shown can happen but you get

209
00:08:19,920 --> 00:08:18,310
a series of organic radicals and luckily

210
00:08:21,000 --> 00:08:19,930
we've already heard a lot about radicals

211
00:08:22,500 --> 00:08:21,010
and essentially what you need to know is

212
00:08:26,040 --> 00:08:22,510
radicals are really reactive they like

213
00:08:28,710 --> 00:08:26,050

to run into things and react and here

214
00:08:31,380 --> 00:08:28,720
I'm showing the oxoacids with their

215
00:08:33,540 --> 00:08:31,390
alkyl tails back again and it's worth

216
00:08:35,010 --> 00:08:33,550
noting that I'm demonstrating that the

217
00:08:37,470 --> 00:08:35,020
hydrogen abstraction has occurred at

218
00:08:39,390 --> 00:08:37,480
this bethe ch2 group but in theory it

219
00:08:41,580 --> 00:08:39,400
could occur anywhere along this alkyl

220
00:08:43,020 --> 00:08:41,590
chain but just for fries the

221
00:08:46,320 --> 00:08:43,030
presentation I'm showing it that way and

222
00:08:48,990 --> 00:08:46,330
so if you have a solution where oxygen

223
00:08:50,790 --> 00:08:49,000
is present or other species you can get

224
00:08:52,140 --> 00:08:50,800
quenching of these radicals or quenching

225
00:08:53,480 --> 00:08:52,150
of the triplet state which will

226
00:08:56,030 --> 00:08:53,490
regenerate your own

227
00:08:57,889 --> 00:08:56,040
oxoacids so that tends to cut down on

228
00:09:00,380 --> 00:08:57,899
how much of the product formation you

229
00:09:01,910 --> 00:09:00,390
see but luckily prebiotic ly we've

230
00:09:04,639 --> 00:09:01,920
established there isn't a lot of oxygen

231
00:09:06,430 --> 00:09:04,649
around and so what you get instead is

232
00:09:09,470 --> 00:09:06,440
recombination to form oligomers

233
00:09:11,300 --> 00:09:09,480
dominating and they are actually

234
00:09:14,960 --> 00:09:11,310
oligomers because I've got both divers

235
00:09:17,389 --> 00:09:14,970
and trimers um and you get this even

236
00:09:19,730 --> 00:09:17,399
especially in low oxygen environments

237
00:09:21,829 --> 00:09:19,740
and so if we look at some actual data

238
00:09:24,889 --> 00:09:21,839

this is just electrospray ionization

239
00:09:27,710 --> 00:09:24,899
mass spec for to oxygen oeq acid

240
00:09:30,500 --> 00:09:27,720
so before fatalis we see the oxy

241
00:09:33,019 --> 00:09:30,510
autonomic acid and it's dial and then

242
00:09:35,300 --> 00:09:33,029
after Fatah lysis the sort of major peak

243
00:09:38,030 --> 00:09:35,310
that we see showing up over here is this

244
00:09:43,190 --> 00:09:38,040
are our tartaric acid derivative so a

245
00:09:45,170 --> 00:09:43,200
double tailed so a double tailed lipid

246
00:09:47,180 --> 00:09:45,180
being formed but you'll notice that

247
00:09:49,400 --> 00:09:47,190
that's not the only product we're

248
00:09:52,070 --> 00:09:49,410
forming so we we did a quite a bit of

249
00:09:54,050 --> 00:09:52,080
mechanistic work to figure out what some

250
00:09:57,260 --> 00:09:54,060
of the other products we were making

251
00:09:59,420 --> 00:09:57,270
were and so there's other possibilities

252
00:10:01,940 --> 00:09:59,430
that can happen so instead of just

253
00:10:04,160 --> 00:10:01,950
getting these radicals you can also have

254
00:10:06,440 --> 00:10:04,170
an intramolecular reaction that

255
00:10:08,870 --> 00:10:06,450
essentially kicks off the alkyl tail and

256
00:10:12,530 --> 00:10:08,880
you regenerate pyruvic acid from your

257
00:10:13,610 --> 00:10:12,540
longer tailed oXXO acid and essentially

258
00:10:15,650 --> 00:10:13,620
there are a couple of different

259
00:10:17,630 --> 00:10:15,660
processes that it can occur where you're

260
00:10:19,449 --> 00:10:17,640
generating multiple photoactive

261
00:10:21,040 --> 00:10:19,459
molecules and these oligomeric

262
00:10:24,139 --> 00:10:21,050
intermediates that are themselves

263
00:10:27,290 --> 00:10:24,149

photoactive so you've started from a

264
00:10:29,269 --> 00:10:27,300
single simple molecule in solution but

265
00:10:31,250 --> 00:10:29,279
you're starting to generate all of these

266
00:10:33,110 --> 00:10:31,260
molecules that can go and do photo

267
00:10:37,579 --> 00:10:33,120
chemistry and cross react with each

268
00:10:38,930 --> 00:10:37,589
other as you as you go and so like this

269
00:10:40,670 --> 00:10:38,940
is one of one of the very simple

270
00:10:42,319 --> 00:10:40,680
examples but you can have the pyruvic

271
00:10:45,710 --> 00:10:42,329
acid that you generated via the norrish

272
00:10:48,019 --> 00:10:45,720
type ii reaction and it can react with

273
00:10:50,000 --> 00:10:48,029
the oxygen oeq acid and you could get

274
00:10:51,829 --> 00:10:50,010
this guy which is still your tartaric

275
00:10:54,590 --> 00:10:51,839
acid derivative but this time you've got

276
00:10:57,410 --> 00:10:54,600
a six carbon tail and a methyl group and

277
00:10:59,630 --> 00:10:57,420
so there are series of reactions that

278
00:11:01,670 --> 00:10:59,640
can happen like that and so this is as

279
00:11:04,819 --> 00:11:01,680
close to messy chemistry as a physical

280
00:11:07,120 --> 00:11:04,829
chemist is willing to get but you end up

281
00:11:10,810 --> 00:11:07,130
with a series of different isomers

282
00:11:14,680 --> 00:11:10,820
with sing or different different

283
00:11:19,750 --> 00:11:14,690
molecules with one to two to three multi

284
00:11:24,700 --> 00:11:19,760
tails tails for your oligomers that are

285
00:11:26,020 --> 00:11:24,710
forming and all of these and I should

286
00:11:27,490 --> 00:11:26,030
say that all of these could be slightly

287
00:11:28,630 --> 00:11:27,500
different isomers because with mass spec

288
00:11:33,850 --> 00:11:28,640

you you can't tell the difference

289
00:11:35,650 --> 00:11:33,860
between the two but yeah and so we've

290
00:11:37,510 --> 00:11:35,660
got this series of multi tailed

291
00:11:41,230 --> 00:11:37,520
photochemical products and it's sort of

292
00:11:43,420 --> 00:11:41,240
very easy to see this ready formation of

293
00:11:48,220 --> 00:11:43,430
multi tailed lipids even from a simple

294
00:11:50,140 --> 00:11:48,230
single single tailed precursor and then

295
00:11:52,810 --> 00:11:50,150
of course we also have this tartaric

296
00:11:54,370 --> 00:11:52,820
acid derivative which is the main the

297
00:11:57,910 --> 00:11:54,380
main product that we see in the mass

298
00:11:59,290 --> 00:11:57,920
spec and then those of you who are

299
00:12:02,890 --> 00:11:59,300
keeping track at home this is the fourth

300
00:12:04,540 --> 00:12:02,900
year I've put this slide up but as we do

301
00:12:07,120 --> 00:12:04,550
this photo chemistry we also see

302
00:12:08,740 --> 00:12:07,130
self-assembly and so we start with a

303
00:12:10,930 --> 00:12:08,750
clear solution that's below the

304
00:12:14,350 --> 00:12:10,940
aggregation concentration of the lipids

305
00:12:17,410 --> 00:12:14,360
and as fatah lysis proceeds the solution

306
00:12:19,120 --> 00:12:17,420
gets cloudy and we're forming we're

307
00:12:21,130 --> 00:12:19,130
forming aggregates that are spherical in

308
00:12:25,090 --> 00:12:21,140
shape and mono disbursement size and

309
00:12:26,500 --> 00:12:25,100
they're too big to be well so they're

310
00:12:27,960 --> 00:12:26,510
they're too big to sort of be what you

311
00:12:31,150 --> 00:12:27,970
would classically think of as a micelle

312
00:12:33,640 --> 00:12:31,160
and so we have posited in the past that

313
00:12:36,640 --> 00:12:33,650

they are vesicles we've been working to

314
00:12:38,500 --> 00:12:36,650
characterize those more I think it's

315
00:12:39,670 --> 00:12:38,510
worth pointing out that even if they

316
00:12:42,670 --> 00:12:39,680
aren't vesicles it's an interesting

317
00:12:44,350 --> 00:12:42,680
regime of self-assembly where you're

318
00:12:46,750 --> 00:12:44,360
getting these colloidal aggregates that

319
00:12:48,820 --> 00:12:46,760
are mono dispersed in size and spherical

320
00:12:51,160 --> 00:12:48,830
and that lasts for years

321
00:12:53,740 --> 00:12:51,170
in solution so we're sort of working on

322
00:12:56,290 --> 00:12:53,750
that I can add that this happens even

323
00:12:58,360 --> 00:12:56,300
for you're really short to oXXO hexanoic

324
00:13:00,580 --> 00:12:58,370
acid which only has a four carbon tail

325
00:13:02,260 --> 00:13:00,590
as you do Fatah lysis and get these

326
00:13:04,120 --> 00:13:02,270
double tailed or multi tailed products

327
00:13:07,780 --> 00:13:04,130
you see this aggregation occurring as

328
00:13:10,000 --> 00:13:07,790
well and and you see that for the

329
00:13:12,790 --> 00:13:10,010
mixture of oxygen - ox o decanoic acid

330
00:13:15,120 --> 00:13:12,800
we don't see this for pyruvic for for

331
00:13:18,460 --> 00:13:15,130
obvious reasons it's just too short and

332
00:13:20,090 --> 00:13:18,470
I'm working on getting some more

333
00:13:23,000 --> 00:13:20,100
information

334
00:13:24,410 --> 00:13:23,010
about this and I should have if I come

335
00:13:25,700 --> 00:13:24,420
back next year this shouldn't be the

336
00:13:27,260 --> 00:13:25,710
same slide anymore because we've got

337
00:13:31,070 --> 00:13:27,270
some good stuff coming it's just not

338
00:13:33,830 --> 00:13:31,080

quite ready to to share yet um and yeah

339
00:13:36,320 --> 00:13:33,840
and so basically we've been making a

340
00:13:39,350 --> 00:13:36,330
we're sort of exploring this path to

341
00:13:41,450 --> 00:13:39,360
making other molecules with with

342
00:13:45,050 --> 00:13:41,460
sunlight and sort of a very ready

343
00:13:48,200 --> 00:13:45,060
synthesis of multi tailed lipids from

344
00:13:50,150 --> 00:13:48,210
simple periodically relevant precursors

345
00:13:53,060 --> 00:13:50,160
so with that I just like to acknowledge

346
00:14:06,380 --> 00:13:53,070
a group and all of the funding and I'm

347
00:14:08,030 --> 00:14:06,390
happy to take any questions well I got a

348
00:14:09,410 --> 00:14:08,040
question on the way you have any idea

349
00:14:11,510 --> 00:14:09,420
what sort of yields are getting from

350
00:14:13,220 --> 00:14:11,520
this um so we think we're getting so

351
00:14:15,530 --> 00:14:13,230
it's a little hard to tell with it's

352
00:14:19,040 --> 00:14:15,540
easier to tell with pyruvic because the

353
00:14:22,730 --> 00:14:19,050
NMR is much simpler and so with pyruvic

354
00:14:25,340 --> 00:14:22,740
acid under anaerobic conditions for five

355
00:14:28,550 --> 00:14:25,350
hours we get about 90% of the pyruvic

356
00:14:30,530 --> 00:14:28,560
acid is consumed for the oxoacids itself

357
00:14:34,280 --> 00:14:30,540
for the longer tailed ones it's probably

358
00:14:36,050 --> 00:14:34,290
closer to about 30% but it's also harder

359
00:14:39,350 --> 00:14:36,060
to tell so the error bars on that yield

360
00:14:40,880 --> 00:14:39,360
are yeah yeah and that we can really

361
00:14:43,070 --> 00:14:40,890
only monitor the decrease in the

362
00:14:45,320 --> 00:14:43,080
starting material so I don't know the I

363
00:14:48,970 --> 00:14:45,330

don't know the ratio other than relative

364
00:14:52,550 --> 00:14:48,980
mass spec of the products we're making

365
00:14:55,910 --> 00:14:52,560
yeah so the first question is related to

366
00:15:00,010 --> 00:14:55,920
our PWR proposal so if you have ever

367
00:15:03,350 --> 00:15:00,020
experienced the any sort of UV effect on

368
00:15:05,780 --> 00:15:03,360
vesicles so if you know if something

369
00:15:08,000 --> 00:15:05,790
happens on vesicles already formed when

370
00:15:10,310 --> 00:15:08,010
you shine light on them and then I have

371
00:15:13,880 --> 00:15:10,320
another question so we have seen that

372
00:15:16,730 --> 00:15:13,890
phospholipids have two tails so I was

373
00:15:19,850 --> 00:15:16,740
wondering do you think that we

374
00:15:22,850 --> 00:15:19,860
envisioned it was for elation reaction

375
00:15:25,910 --> 00:15:22,860
happening after the formation of a

376
00:15:29,350 --> 00:15:25,920
double tail fatty acid or would you

377
00:15:33,410 --> 00:15:29,360
consider do you think that it first

378
00:15:36,080 --> 00:15:33,420
first a fatty acid is phosphorylated and

379
00:15:38,120 --> 00:15:36,090
it forms the second day yeah so with the

380
00:15:40,010 --> 00:15:38,130
with the sort of first question I

381
00:15:41,870 --> 00:15:40,020
haven't done any work sort of on

382
00:15:44,960 --> 00:15:41,880
vesicles and doing photochemistry on

383
00:15:47,120 --> 00:15:44,970
sort of preformed vesicles although it

384
00:15:48,830 --> 00:15:47,130
it would be interesting and I have some

385
00:15:51,440 --> 00:15:48,840
results that I didn't talk about where

386
00:15:55,070 --> 00:15:51,450
you can also get the cross reaction with

387
00:15:57,230 --> 00:15:55,080
the photoactive oxyacid and a fatty acid

388
00:15:58,370 --> 00:15:57,240

and you can get that cross cross product

389
00:16:00,470 --> 00:15:58,380
as well

390
00:16:02,150 --> 00:16:00,480
so I don't really have an answer to your

391
00:16:04,580 --> 00:16:02,160
first question because I haven't really

392
00:16:09,770 --> 00:16:04,590
done anything with it as to the second

393
00:16:12,620 --> 00:16:09,780
one um let's see uh what was it again

394
00:16:13,880 --> 00:16:12,630
scar I had an answer that it disappeared

395
00:16:15,470 --> 00:16:13,890
yeah if you think that the

396
00:16:18,980 --> 00:16:15,480
phosphorylation reaction happened oh

397
00:16:20,930 --> 00:16:18,990
right right um so I think it would be

398
00:16:22,520 --> 00:16:20,940
hard to phosphorylate the starting

399
00:16:23,870 --> 00:16:22,530
material of the oxoacids because it is

400
00:16:25,490 --> 00:16:23,880
so molecule specific you're going to

401
00:16:27,730 --> 00:16:25,500
change the electronic structure and so

402
00:16:29,750 --> 00:16:27,740
the the mechanistic you know the

403
00:16:33,140 --> 00:16:29,760
excitation and then the photochemistry

404
00:16:34,610 --> 00:16:33,150
that happens may not be the same Bradley

405
00:16:37,430 --> 00:16:34,620
would know more about phosphorylating

406
00:16:39,320 --> 00:16:37,440
the products I think even if you could

407
00:16:40,970 --> 00:16:39,330
phosphorylate the products as we were

408
00:16:42,860 --> 00:16:40,980
talking about earlier the issue is going

409
00:16:44,930 --> 00:16:42,870
to be adding the choline group um I

410
00:16:47,870 --> 00:16:44,940
think because I don't really know how

411
00:16:51,860 --> 00:16:47,880
that would happen yeah

412
00:16:54,880 --> 00:16:51,870
hi I'm just curious about the whether

413
00:16:58,040 --> 00:16:54,890

there is any published or unpublished

414
00:17:01,520 --> 00:16:58,050
robotically available pathways for the

415
00:17:04,580 --> 00:17:01,530
alpha keto acids yeah you proposed

416
00:17:08,900 --> 00:17:04,590
that's my first question and the second

417
00:17:12,170 --> 00:17:08,910
question is when you talk about the

418
00:17:13,790 --> 00:17:12,180
alpha keto acids forming these vesicle

419
00:17:17,060 --> 00:17:13,800
like structure do you know if they're

420
00:17:20,300 --> 00:17:17,070
multilamellar or uni lam lore type of

421
00:17:23,330 --> 00:17:20,310
vesicles yeah yeah okay so the the first

422
00:17:25,400 --> 00:17:23,340
part um so pyruvic acid is a very

423
00:17:28,160 --> 00:17:25,410
probiotic lis relevant molecules at the

424
00:17:29,390 --> 00:17:28,170
shortest one and you can make it in

425
00:17:31,520 --> 00:17:29,400
hydrothermal vents you can make it a

426
00:17:32,990 --> 00:17:31,530
bunch of different ways um and it's been

427
00:17:36,050 --> 00:17:33,000
seen in meteorites and things like that

428
00:17:36,860 --> 00:17:36,060
I believe other oxoacids have also been

429
00:17:38,720 --> 00:17:36,870
seen in meteorites

430
00:17:40,610 --> 00:17:38,730
perhaps not these ones with the alkyl

431
00:17:42,470 --> 00:17:40,620
tails but they are also the right length

432
00:17:45,660 --> 00:17:42,480
for sort of a fisher fisher Tropes

433
00:17:46,980 --> 00:17:45,670
type synthesis as well so i

434
00:17:49,050 --> 00:17:46,990
say a hundred percent that these

435
00:17:50,070 --> 00:17:49,060
specific oxoacids have been seen

436
00:17:53,910 --> 00:17:50,080
periodically but they're certainly

437
00:17:57,780 --> 00:17:53,920
probiotic ly reasonable and then the

438
00:17:59,280 --> 00:17:57,790

second question was oh just talking

439
00:18:01,020 --> 00:17:59,290
about whether we know that they're

440
00:18:06,090 --> 00:18:01,030
lamellar or not we haven't been able to

441
00:18:08,130 --> 00:18:06,100
characterize well we we've been trying

442
00:18:10,140 --> 00:18:08,140
for a long time to get access to a cryo

443
00:18:11,730 --> 00:18:10,150
em2 to see the lamellar structure so we

444
00:18:17,340 --> 00:18:11,740
I don't have any information for you

445
00:18:20,310 --> 00:18:17,350
about that um yeah I don't know I I want

446
00:18:24,900 --> 00:18:20,320
talks about a time of exposure in the

447
00:18:27,690 --> 00:18:24,910
photochemical reaction yeah so of for

448
00:18:30,900 --> 00:18:27,700
how many seconds or minutes or hours you

449
00:18:33,240 --> 00:18:30,910
exposed these biomolecules for further

450
00:18:36,450 --> 00:18:33,250
activation because in evolutionary

451
00:18:39,960 --> 00:18:36,460
history earth was our biomolecules are

452
00:18:43,170 --> 00:18:39,970
we're exposed for the that kind of

453
00:18:45,840 --> 00:18:43,180
physical things for a long period so

454
00:18:48,210 --> 00:18:45,850
what is a probable effect of in we

455
00:18:50,880 --> 00:18:48,220
expose biomolecules for that kind of

456
00:18:53,280 --> 00:18:50,890
physical parameters yeah so so these

457
00:18:56,280 --> 00:18:53,290
particular experiments are five hours

458
00:18:58,800 --> 00:18:56,290
long in the 450 watt xenon arc lamp

459
00:19:01,620 --> 00:18:58,810
that's picked mainly because I can do

460
00:19:03,720 --> 00:19:01,630
that reaction in a day um because it

461
00:19:05,900 --> 00:19:03,730
just works out better um the the

462
00:19:08,220 --> 00:19:05,910
interesting thing to note is that

463
00:19:11,070 --> 00:19:08,230

because stability of your products is

464
00:19:14,790 --> 00:19:11,080
always going to be a question so these

465
00:19:16,620 --> 00:19:14,800
products here with the oxoacids absorb

466
00:19:18,690 --> 00:19:16,630
light but you'll notice that that Axio

467
00:19:20,220 --> 00:19:18,700
acid functionality is not in the

468
00:19:21,420 --> 00:19:20,230
products so they're they don't have

469
00:19:23,820 --> 00:19:21,430
chromophore so they're not going to

470
00:19:26,550 --> 00:19:23,830
absorb light in that near UV region so

471
00:19:28,830 --> 00:19:26,560
they ought to be relatively stable and

472
00:19:30,600 --> 00:19:28,840
UV protected I mean not from really

473
00:19:35,670 --> 00:19:30,610
high-intensity UV light from but at

474
00:19:39,190 --> 00:19:35,680
least from sort of near UV light no no