EARTH-LIFE
SCIENCE
INSTITUTE

Marc Koper

Proton-coupled Electron Transfer & the Electrocatalysis of CO_2 Reduction

```
1
00:00:00,720 --> 00:00:11,190
[Music]

2
00:00:18,600 --> 00:00:16,150
thank you and thank you for inviting me

3
00:00:20,800 --> 00:00:18,610
and letting me be part of this of this

4
00:00:23,260 --> 00:00:20,810
symposium and I should specifically

5
00:00:25,870 --> 00:00:23,270
thank Nakamura sound for inviting me

6
00:00:28,060 --> 00:00:25,880
actually I'm I'm a physical electric

7
00:00:30,580 --> 00:00:28,070
chemist and and before this morning I

8
00:00:32,500 --> 00:00:30,590
never actually thought about the origin

9
00:00:34,840 --> 00:00:32,510
of life so I am not sure if I will have

10
00:00:38,740 --> 00:00:34,850
anything to tell you about the origin of

11
00:00:40,270 --> 00:00:38,750
life but yeah if you don't find this

12
00:00:44,890 --> 00:00:40,280
useful you can you can blame

13
00:00:47,380 --> 00:00:44,900
```

nakamura-san afterwards since I work on

14
00:00:49,210 --> 00:00:47,390
in the area of electric Italia's and

15
00:00:52,090 --> 00:00:49,220
this is what Nakamura Sound asked me to

16
00:00:54,070 --> 00:00:52,100
talk about and specifically a part of my

17
00:00:57,969 --> 00:00:54,080
group works on on the electric Attalla

18
00:01:00,060 --> 00:00:57,979
C's of co2 reduction and and and the

19
00:01:03,759 --> 00:01:00,070
relation with proton coupled electron

20
00:01:05,109 --> 00:01:03,769
transfer and maybe it's useful to to

21
00:01:07,719 --> 00:01:05,119
explain a little bit of a how an

22
00:01:10,359 --> 00:01:07,729
electric chemist looks at redox

23
00:01:13,359 --> 00:01:10,369
reactions or how we study them so the

24
00:01:15,130 --> 00:01:13,369
way I study redox reactions in

25
00:01:16,690 --> 00:01:15,140
electrochemical cell is that I have an

26
00:01:20,200 --> 00:01:16,700
electrode and the electrode is typically

27
00:01:24,640 --> 00:01:20,210
also that catalyst for my reaction and I

28
00:01:28,150 --> 00:01:24,650
apply a potential using a basically an

29
00:01:30,490 --> 00:01:28,160
electronic feedback a piece of equipment

30
00:01:32,050 --> 00:01:30,500
called a potential stab and with that

31
00:01:35,560 --> 00:01:32,060
piece of equipment I can change the

32
00:01:37,450 --> 00:01:35,570
electrode potential of my electrode from

33
00:01:39,370 --> 00:01:37,460
reducing which would be a very negative

34
00:01:41,500 --> 00:01:39,380
potential to oxidizing which would be a

35
00:01:42,820 --> 00:01:41,510
very positive potential and then I

36
00:01:44,350 --> 00:01:42,830
measure the current that is flowing

37
00:01:46,899 --> 00:01:44,360
through that electrode and that current

38
00:01:48,730 --> 00:01:46,909

gives me the rate of the reaction and in

39
00:01:52,390 --> 00:01:48,740
that way I can generate current voltage

40
00:01:54,580 --> 00:01:52,400
curves of redox reactions and and then

41
00:01:56,020 --> 00:01:54,590
if I study a particular redox reaction

42
00:01:59,020 --> 00:01:56,030
obviously I will need to know where

43
00:02:00,340 --> 00:01:59,030
where let's say the redox potential the

44
00:02:02,980 --> 00:02:00,350
equilibrium redox potential of that

45
00:02:06,670 --> 00:02:02,990
redox reaction is and in typically if I

46
00:02:08,559 --> 00:02:06,680
would reduce co2 I would I would ideally

47
00:02:10,690 --> 00:02:08,569
see some current flowing and and

48
00:02:12,809 --> 00:02:10,700
reduction current in electrochemistry we

49
00:02:15,430 --> 00:02:12,819
consider it a negative current flowing

50
00:02:17,199 --> 00:02:15,440
if I as I make the potential more

51
00:02:18,640 --> 00:02:17,209
negative I would expect some reduction

52
00:02:20,500 --> 00:02:18,650
current to start flowing and then this

53
00:02:22,660 --> 00:02:20,510
current potential curve would would

54
00:02:24,300 --> 00:02:22,670
typically look something like this and

55
00:02:26,230 --> 00:02:24,310
this is then what I'm

56
00:02:28,930 --> 00:02:26,240
electrochemically and if I reduce co2

57
00:02:30,310 --> 00:02:28,940
then I I can make a number of different

58
00:02:32,260 --> 00:02:30,320
products and we've seen some of those

59
00:02:33,940 --> 00:02:32,270
already today and obviously from the

60
00:02:35,770 --> 00:02:33,950
current I can't really tell what product

61
00:02:37,900 --> 00:02:35,780
I'm I'm making I can just tell how many

62
00:02:42,280 --> 00:02:37,910
electrons are flowing in the external

63
00:02:44,560 --> 00:02:42,290

circuit and then I have a number of

64
00:02:46,570 --> 00:02:44,570
important things that I look at I mean

65
00:02:48,910 --> 00:02:46,580
typically we would like this to happen

66
00:02:50,620 --> 00:02:48,920
very close to the redox potential

67
00:02:52,810 --> 00:02:50,630
because my interest is actually not so

68
00:02:55,780 --> 00:02:52,820
much in in the origin of life but my

69
00:02:57,700 --> 00:02:55,790
interest is in seeing if I can use co2

70
00:02:59,380 --> 00:02:57,710
and water and renewable electricity to

71
00:03:00,820 --> 00:02:59,390
make interesting molecules and I would

72
00:03:02,770 --> 00:03:00,830
like to do that as efficiently as

73
00:03:04,540 --> 00:03:02,780
possible and that means that I would

74
00:03:06,970 --> 00:03:04,550
like this to happen as close as possible

75
00:03:09,160 --> 00:03:06,980
to the equilibrium potential that this

76
00:03:10,420 --> 00:03:09,170
typically doesn't happen and it means

77
00:03:11,830 --> 00:03:10,430
that in order to get some kind of

78
00:03:14,170 --> 00:03:11,840
current we need to move the potential

79
00:03:16,720 --> 00:03:14,180
away from the standard redox potential

80
00:03:18,640 --> 00:03:16,730
we call that an over potential and if

81
00:03:20,260 --> 00:03:18,650
that over potential is very small then

82
00:03:22,480 --> 00:03:20,270
basically I have a very good catalyst

83
00:03:23,740 --> 00:03:22,490
and if that over potentials very large

84
00:03:26,230 --> 00:03:23,750
then basically I have a very bad

85
00:03:28,150 --> 00:03:26,240
catalyst and much of what we do in

86
00:03:30,220 --> 00:03:28,160
electric at alysus is to find electrode

87
00:03:32,110 --> 00:03:30,230
materials that that make this over

88
00:03:33,640 --> 00:03:32,120

potential very very small but obviously

89
00:03:35,050 --> 00:03:33,650
I also need to worry about the product

90
00:03:39,130 --> 00:03:35,060
that I makes I also need to worry about

91
00:03:41,560 --> 00:03:39,140
the selectivity now if I would not do

92
00:03:44,140 --> 00:03:41,570
this electro chemically but I need some

93
00:03:46,810 --> 00:03:44,150
other kind of voltage source I would

94
00:03:49,330 --> 00:03:46,820
probably use another redox couple to

95
00:03:51,640 --> 00:03:49,340
basically donate the electrons to reduce

96
00:03:53,050 --> 00:03:51,650
co2 and that would be d let's say the

97
00:03:54,580 --> 00:03:53,060
other redox couple hydrogen would be

98
00:03:56,620 --> 00:03:54,590
would be a good example and obviously

99
00:03:58,240 --> 00:03:56,630
this redox couple needs to have an a

100
00:04:01,570 --> 00:03:58,250
redox potential that is more negative

101
00:04:03,670 --> 00:04:01,580
than the redox potential of the of the

102
00:04:06,670 --> 00:04:03,680
species that I'm trying to to reduce and

103
00:04:09,370 --> 00:04:06,680
and then in in corrosion Theory we don't

104
00:04:11,410 --> 00:04:09,380
basically we define that we we make this

105
00:04:12,910 --> 00:04:11,420
mixed potential where the current of the

106
00:04:15,160 --> 00:04:12,920
oxidation reaction and the current of

107
00:04:16,780 --> 00:04:15,170
the reduction reaction is equal and then

108
00:04:21,849 --> 00:04:16,790
we end up at this sort of mixed

109
00:04:25,120 --> 00:04:21,859
potential where everything happens now

110
00:04:26,980 --> 00:04:25,130
before I move on to try and explain how

111
00:04:28,840 --> 00:04:26,990
these reactions take place and how I can

112
00:04:30,250 --> 00:04:28,850
make good catalyst for this and and how

113
00:04:33,040 --> 00:04:30,260

what is the role of protons and

114
00:04:35,590 --> 00:04:33,050
electrons there's one thing that that I

115
00:04:37,830 --> 00:04:35,600
included as a slide because of the the

116
00:04:40,480 --> 00:04:37,840
talk that we heard this morning

117
00:04:43,270 --> 00:04:40,490
oscillations because that actually turns

118
00:04:46,510 --> 00:04:43,280
out to be my previous life I did a PhD

119
00:04:48,460 --> 00:04:46,520
in in in in studying electrochemical

120
00:04:50,530 --> 00:04:48,470
oscillations and instabilities and

121
00:04:52,390 --> 00:04:50,540
typically what you would expect if you

122
00:04:54,969 --> 00:04:52,400
apply a fixed potential that after a

123
00:04:56,409 --> 00:04:54,979
while you would expect to get a a

124
00:04:57,730 --> 00:04:56,419
constant current a steady state current

125
00:05:00,189 --> 00:04:57,740
or if you apply and this is something

126
00:05:01,930 --> 00:05:00,199
that we can do also with our feedback

127
00:05:03,580 --> 00:05:01,940
electronics we can apply a constant

128
00:05:06,820 --> 00:05:03,590
current and they would expect that the

129
00:05:08,950 --> 00:05:06,830
system develops a stable potential but

130
00:05:10,779 --> 00:05:08,960
this very often doesn't happen and is

131
00:05:12,700 --> 00:05:10,789
typically what what we see is sometimes

132
00:05:14,830 --> 00:05:12,710
that when these curves do not look

133
00:05:17,350 --> 00:05:14,840
sigmoidal like this but develop a branch

134
00:05:19,450 --> 00:05:17,360
where we have a negative resistance or a

135
00:05:22,240 --> 00:05:19,460
negative impedance then we can develop

136
00:05:25,240 --> 00:05:22,250
instabilities and these instabilities

137
00:05:28,180 --> 00:05:25,250
can give rise to oscillations and and

138
00:05:30,610 --> 00:05:28,190

and I show you a few here and these are

139
00:05:33,189 --> 00:05:30,620
really relatively simple reactions this

140
00:05:35,320 --> 00:05:33,199
is the reduction of indium 3 plus on on

141
00:05:36,969 --> 00:05:35,330
a mercury electrode and I will not go

142
00:05:38,350 --> 00:05:36,979
into the details but this was some a

143
00:05:40,480 --> 00:05:38,360
question I think that was asked this

144
00:05:42,250 --> 00:05:40,490
morning if you can develop something

145
00:05:45,219 --> 00:05:42,260
like chaos here you see the current

146
00:05:47,920 --> 00:05:45,229
oscillate in the reduction of indium on

147
00:05:50,020 --> 00:05:47,930
a mercury electrode and and this this is

148
00:05:52,360 --> 00:05:50,030
how we how we drew what is called a

149
00:05:54,129 --> 00:05:52,370
strange attractor from this from these

150
00:05:55,450 --> 00:05:54,139
these oscillations you can see here a

151
00:05:57,279 --> 00:05:55,460
return map I don't know if you're

152
00:05:58,650 --> 00:05:57,289
familiar with this kind of terminology

153
00:06:01,990 --> 00:05:58,660
but what we see here is a

154
00:06:04,420 --> 00:06:02,000
deterministically chaotic oscillation in

155
00:06:05,950 --> 00:06:04,430
the reduction of indium three-plus on a

156
00:06:07,870 --> 00:06:05,960
mercury electrode and this develops

157
00:06:10,270 --> 00:06:07,880
through a series of period doubling

158
00:06:12,040 --> 00:06:10,280
bifurcation and you can have very

159
00:06:13,930 --> 00:06:12,050
complicated oscillations here we see

160
00:06:15,339 --> 00:06:13,940
something that people call bursting

161
00:06:16,570 --> 00:06:15,349
oscillations this is the reduction of

162
00:06:18,730 --> 00:06:16,580
hydrogen peroxide on a platinum

163
00:06:20,110 --> 00:06:18,740

electrode and now we drive this as a

164
00:06:22,629 --> 00:06:20,120
constant current that we measure the

165
00:06:23,860 --> 00:06:22,639
voltage and you see that it seems to go

166
00:06:26,110 --> 00:06:23,870
through two different types of

167
00:06:27,730 --> 00:06:26,120
oscillations one with a very high

168
00:06:30,610 --> 00:06:27,740
frequency and one with a lower frequency

169
00:06:32,379 --> 00:06:30,620
and I don't want to dwell on this but

170
00:06:33,879 --> 00:06:32,389
this this really much of this can be

171
00:06:35,529 --> 00:06:33,889
understood simply from the current

172
00:06:38,260 --> 00:06:35,539
voltage curve where we have a region of

173
00:06:39,909 --> 00:06:38,270
negative impedance that is coupled to

174
00:06:42,010 --> 00:06:39,919
the external circuit and that is coupled

175
00:06:43,560 --> 00:06:42,020
to a slow feedback mechanism which is

176
00:06:45,520 --> 00:06:43,570
very important in these type of

177
00:06:48,120 --> 00:06:45,530
instabilities and in this case the slow

178
00:06:50,709 --> 00:06:48,130
feedback mechanism is mass transport and

179
00:06:51,159 --> 00:06:50,719
actually we showed in a very simple

180
00:06:53,529 --> 00:06:51,169
model

181
00:06:55,360 --> 00:06:53,539
here many years ago and this was during

182
00:06:57,969 --> 00:06:55,370
my PhD that we can understand much of

183
00:07:00,459 --> 00:06:57,979
what is happening in this in this this

184
00:07:02,140 --> 00:07:00,469
implies by simply coupling the the

185
00:07:03,670 --> 00:07:02,150
kinetics that give rise to the negative

186
00:07:04,830 --> 00:07:03,680
impedance to mass transport and that

187
00:07:07,869 --> 00:07:04,840
will give you rise to oscillations

188
00:07:09,189 --> 00:07:07,879

instabilities and all the transitions to

189
00:07:11,200 --> 00:07:09,199
chaos that we see so the chemistry

190
00:07:14,399 --> 00:07:11,210
behind that is relatively simple what we

191
00:07:16,689 --> 00:07:14,409
have here is a very simple in

192
00:07:18,249 --> 00:07:16,699
non-linearity that is coupled to a slow

193
00:07:22,029 --> 00:07:18,259
feedback mechanism and that can give

194
00:07:23,110 --> 00:07:22,039
rise to these type of instabilities but

195
00:07:25,329 --> 00:07:23,120
that is not what I want to talk about

196
00:07:27,540 --> 00:07:25,339
what I want to talk about is about how

197
00:07:29,980 --> 00:07:27,550
to catalyze electron transfer reactions

198
00:07:34,540 --> 00:07:29,990
and one thing you may have noticed if we

199
00:07:36,939 --> 00:07:34,550
if we can allow co2 to let's say CEO or

200
00:07:38,829 --> 00:07:36,949
formic acid or methane or methanol or

201
00:07:40,779 --> 00:07:38,839
ethanol and you will see that these are

202
00:07:42,839 --> 00:07:40,789
things that we can make that this

203
00:07:45,809 --> 00:07:42,849
requires a different number of electrons

204
00:07:48,939 --> 00:07:45,819
and one thing I've learned is that the

205
00:07:50,709 --> 00:07:48,949
overpotential that we typically find to

206
00:07:51,969 --> 00:07:50,719
catalyze a certain reaction depends on

207
00:07:54,489 --> 00:07:51,979
the number of electrons that we're

208
00:07:56,350 --> 00:07:54,499
trying to transfer if we transfer a

209
00:07:58,329 --> 00:07:56,360
single electron and this typically this

210
00:08:00,070 --> 00:07:58,339
is something we would we would model

211
00:08:01,719 --> 00:08:00,080
using a theory that you may have heard

212
00:08:03,820 --> 00:08:01,729
of is a Marcus theory for electron

213
00:08:05,649 --> 00:08:03,830

transfer and the Marcus theory of

214
00:08:08,079 --> 00:08:05,659
electron transfer tells us that the rate

215
00:08:09,999 --> 00:08:08,089
of an electron transfer event depends on

216
00:08:13,029 --> 00:08:10,009
how easy or how difficult it is to

217
00:08:15,279 --> 00:08:13,039
reorganize the environment of the redox

218
00:08:17,320 --> 00:08:15,289
Center basically the solvent if it is

219
00:08:19,329 --> 00:08:17,330
very difficult to reorganize the solvent

220
00:08:21,010 --> 00:08:19,339
then the rate of electron transfer will

221
00:08:23,200 --> 00:08:21,020
be slow if it is easy the rate of

222
00:08:24,519 --> 00:08:23,210
radical transfer will be fast basically

223
00:08:26,139 --> 00:08:24,529
what is saying is the solvent

224
00:08:28,089 --> 00:08:26,149
reorganization or the environmental

225
00:08:30,790 --> 00:08:28,099
Regan ization of the redox Center is

226
00:08:34,240 --> 00:08:30,800
your reaction coordinate that basically

227
00:08:36,159 --> 00:08:34,250
accommodates the electron transfer once

228
00:08:39,459 --> 00:08:36,169
we transfer two electrons things are a

229
00:08:41,259 --> 00:08:39,469
little bit more complicated or maybe I

230
00:08:43,389 --> 00:08:41,269
should say easier because one of the

231
00:08:46,240 --> 00:08:43,399
things that we find from Marcus theory

232
00:08:49,530 --> 00:08:46,250
is it's very unlikely that you transfer

233
00:08:51,819 --> 00:08:49,540
two electrons exactly simultaneously and

234
00:08:53,889 --> 00:08:51,829
and that is because the solvent

235
00:08:56,680 --> 00:08:53,899
basically needs to reorganize too much

236
00:08:59,980 --> 00:08:56,690
and it is practically always more

237
00:09:02,620 --> 00:08:59,990
efficient to to transfer these electrons

238
00:09:04,990 --> 00:09:02,630

one by one so we transfer the first

239
00:09:07,390 --> 00:09:05,000
electron then we generate an intern

240
00:09:10,570 --> 00:09:07,400
idiot and then we transfer the second

241
00:09:12,880 --> 00:09:10,580
electron and once we have to catalyze a

242
00:09:16,030 --> 00:09:12,890
two electron transfer reaction what the

243
00:09:17,980 --> 00:09:16,040
catalyst does it basically allows for

244
00:09:20,140 --> 00:09:17,990
the intermediate to exist and the it

245
00:09:22,710 --> 00:09:20,150
gives this intermediate it generates an

246
00:09:25,750 --> 00:09:22,720
intermediate of the right energy and

247
00:09:27,990 --> 00:09:25,760
this optimization of this intermediate

248
00:09:31,090 --> 00:09:28,000
is really the key to having a good

249
00:09:33,550 --> 00:09:31,100
catalyst and if you get just the right

250
00:09:35,140 --> 00:09:33,560
energy of this intermediate and I'll

251
00:09:37,150 --> 00:09:35,150
show you in a minute what I mean by just

252
00:09:39,370 --> 00:09:37,160
the right energy we can reach a

253
00:09:42,400 --> 00:09:39,380
situation where we have very low over

254
00:09:45,490 --> 00:09:42,410
potential let's say effectively almost

255
00:09:47,830 --> 00:09:45,500
zero and we come to the conclusion that

256
00:09:49,510 --> 00:09:47,840
it is in principle possible to catalyze

257
00:09:51,130 --> 00:09:49,520
two electron transfer actions with the

258
00:09:53,920 --> 00:09:51,140
right catalyst in a way that there is

259
00:09:56,290 --> 00:09:53,930
hardly any over potential that also

260
00:09:59,050 --> 00:09:56,300
means that that catalyst is capable of

261
00:10:01,060 --> 00:09:59,060
catalyzing both the reduction and the

262
00:10:04,570 --> 00:10:01,070
oxidation so in both ways I will refer

263
00:10:07,690 --> 00:10:04,580

to that as reversible catalysis once we

264
00:10:09,370 --> 00:10:07,700
transfer more than two electrons you

265
00:10:11,350 --> 00:10:09,380
could for instance the oxidation of

266
00:10:14,680 --> 00:10:11,360
water to oxygen the oxygen evolution

267
00:10:18,100 --> 00:10:14,690
reaction is a good example it requires

268
00:10:20,170 --> 00:10:18,110
four electrons or six what we what we

269
00:10:21,730 --> 00:10:20,180
see then is that we no longer have a

270
00:10:23,860 --> 00:10:21,740
single intermediate we go through

271
00:10:27,730 --> 00:10:23,870
multiple intermediates in our catalytic

272
00:10:29,740 --> 00:10:27,740
scheme and now we need to optimize every

273
00:10:32,410 --> 00:10:29,750
single intermediate to get our optimal

274
00:10:34,450 --> 00:10:32,420
catalyst and the problem here is those

275
00:10:36,520 --> 00:10:34,460
intermediates are similar and they bind

276
00:10:39,400 --> 00:10:36,530
to the catalyst in a very similar way

277
00:10:40,990 --> 00:10:39,410
that means if we bind one stronger we

278
00:10:43,840 --> 00:10:41,000
will bind the other intermediates

279
00:10:46,829 --> 00:10:43,850
stronger as well and that means that we

280
00:10:49,600 --> 00:10:46,839
cannot optimize all these intermediates

281
00:10:52,540 --> 00:10:49,610
independently they are fixed through

282
00:10:54,610 --> 00:10:52,550
what we call scaling relations and these

283
00:10:57,220 --> 00:10:54,620
scaling relations make it very difficult

284
00:10:59,550 --> 00:10:57,230
to reach a situation where you can have

285
00:11:02,770 --> 00:10:59,560
non zero over potential and that

286
00:11:04,090 --> 00:11:02,780
typically means that for electron or six

287
00:11:05,890 --> 00:11:04,100
electron transfer reactions although

288
00:11:08,530 --> 00:11:05,900

they can be catalyzed by a single

289
00:11:10,240 --> 00:11:08,540
catalyst they practically always have an

290
00:11:12,790 --> 00:11:10,250
over potential it's very difficult to

291
00:11:15,130 --> 00:11:12,800
overcome this is one of the reasons why

292
00:11:17,980 --> 00:11:15,140
it is difficult to do water splitting

293
00:11:18,730 --> 00:11:17,990
and why it is difficult to develop fuel

294
00:11:21,400 --> 00:11:18,740
cells

295
00:11:23,110 --> 00:11:21,410
in a in a fully efficient way because we

296
00:11:24,610 --> 00:11:23,120
have a four electron transfer reaction

297
00:11:26,200 --> 00:11:24,620
there that it's very difficult to

298
00:11:29,740 --> 00:11:26,210
catalyze because it has more than one

299
00:11:33,070 --> 00:11:29,750
intermediate and you will see that that

300
00:11:37,720 --> 00:11:33,080
these ideas also apply to co2 reduction

301
00:11:40,780 --> 00:11:37,730
just the same thing but now in in in a

302
00:11:42,100 --> 00:11:40,790
in a way that maybe you recognize from

303
00:11:43,750 --> 00:11:42,110
that from the Marcus theory in the

304
00:11:46,090 --> 00:11:43,760
Marcus theory we have these different

305
00:11:47,590 --> 00:11:46,100
oxidation states of the system we draw

306
00:11:49,390 --> 00:11:47,600
the free energy as a function of the

307
00:11:51,220 --> 00:11:49,400
reaction coordinate we have these

308
00:11:52,990 --> 00:11:51,230
parabolas this is the initial state of

309
00:11:54,820 --> 00:11:53,000
the system this is the final state and

310
00:11:57,250 --> 00:11:54,830
this is our intermediate state now you

311
00:11:59,620 --> 00:11:57,260
can see that if we try to transfer two

312
00:12:01,050 --> 00:11:59,630
electrons simultaneously the activation

313
00:12:03,340 --> 00:12:01,060

energy here is going to be the

314
00:12:04,510 --> 00:12:03,350
intersection of these two parabolas it's

315
00:12:06,100 --> 00:12:04,520
going to be somewhere here so that

316
00:12:08,530 --> 00:12:06,110
activation energy is very high because

317
00:12:11,500 --> 00:12:08,540
we need to reorganize the environment

318
00:12:14,410 --> 00:12:11,510
too much so it makes sense to find this

319
00:12:16,810 --> 00:12:14,420
intermediate oxidation oxidation state

320
00:12:18,070 --> 00:12:16,820
to generate this extra this extra

321
00:12:21,220 --> 00:12:18,080
minimum here in the potential energy

322
00:12:23,590 --> 00:12:21,230
landscape and now here you see the

323
00:12:25,510 --> 00:12:23,600
activation energy of the separate steps

324
00:12:27,370 --> 00:12:25,520
and now what determines a good catalyst

325
00:12:29,140 --> 00:12:27,380
is not so much actually the activation

326
00:12:32,530 --> 00:12:29,150
energy that we have here but it is the

327
00:12:35,710 --> 00:12:32,540
level of this intermediate energy it can

328
00:12:37,750 --> 00:12:35,720
be high it can be low and what I'm going

329
00:12:41,500 --> 00:12:37,760
to argue with is that the best catalyst

330
00:12:43,750 --> 00:12:41,510
will actually will will place this

331
00:12:46,030 --> 00:12:43,760
energy level here exactly at the same

332
00:12:48,430 --> 00:12:46,040
energy as the initial in the final state

333
00:12:50,310 --> 00:12:48,440
so we generate this flat thermodynamic

334
00:12:52,960 --> 00:12:50,320
landscape that is going to be our

335
00:12:55,720 --> 00:12:52,970
optimal catalyst and that is basically

336
00:12:57,550 --> 00:12:55,730
just an expression of a principle that

337
00:12:59,830 --> 00:12:57,560
is known in heterogeneous catalysis is a

338
00:13:01,720 --> 00:12:59,840

subbatch a principle the catalyst should

339
00:13:03,280 --> 00:13:01,730
not bind this intermediate to weakly it

340
00:13:05,560 --> 00:13:03,290
should not bind it to strongly it should

341
00:13:07,000 --> 00:13:05,570
bind it at an intermediate energy level

342
00:13:09,010 --> 00:13:07,010
that basically means it close to

343
00:13:10,990 --> 00:13:09,020
iquilibrium the energy of the

344
00:13:13,000 --> 00:13:11,000
intermediate has to be equal to the

345
00:13:14,800 --> 00:13:13,010
energy of the initial and the final

346
00:13:18,160 --> 00:13:14,810
state and so that gives us a very clear

347
00:13:19,630 --> 00:13:18,170
quantitative argument of how to find the

348
00:13:20,830 --> 00:13:19,640
best catalyst basically we just need to

349
00:13:22,360 --> 00:13:20,840
find a catalyst that binds that

350
00:13:25,510 --> 00:13:22,370
intermediate with just the right energy

351
00:13:27,220 --> 00:13:25,520
and and nowadays it's possible to

352
00:13:28,720 --> 00:13:27,230
calculate energies of intermediates

353
00:13:30,640 --> 00:13:28,730
using quantum chemistry using density

354
00:13:31,700 --> 00:13:30,650
functional Theory calculations for

355
00:13:33,440 --> 00:13:31,710
instance and

356
00:13:35,300 --> 00:13:33,450
allow you to screen many many different

357
00:13:37,160 --> 00:13:35,310
catalysts and this is a way to search

358
00:13:38,720 --> 00:13:37,170
using the computer to search for a good

359
00:13:40,760 --> 00:13:38,730
catalyst and this is a this is a

360
00:13:43,190 --> 00:13:40,770
strategy that is used very much nowadays

361
00:13:46,310 --> 00:13:43,200
in in heterogeneous catalysis and also

362
00:13:47,660 --> 00:13:46,320
in electric Attalla C's now other than

363
00:13:50,450 --> 00:13:47,670

that we're transferring electrons were

364
00:13:51,770 --> 00:13:50,460
also transferring protons and this

365
00:13:55,280 --> 00:13:51,780
brings basically this brings another

366
00:13:56,930 --> 00:13:55,290
reaction coordinate so what I'm assuming

367
00:13:58,670 --> 00:13:56,940
in many cases that when you're

368
00:13:59,930 --> 00:13:58,680
transferring a proton one electron and

369
00:14:01,700 --> 00:13:59,940
what many people assume in the

370
00:14:03,290 --> 00:14:01,710
literature is it is when you're

371
00:14:05,480 --> 00:14:03,300
transferring both the proton and

372
00:14:07,460 --> 00:14:05,490
electron that this happens concertedly

373
00:14:10,400 --> 00:14:07,470
so we transfer a proton and an electron

374
00:14:12,950 --> 00:14:10,410
conservatively so we go from a to a h

375
00:14:14,690 --> 00:14:12,960
and so to understand the thermodynamics

376
00:14:16,310 --> 00:14:14,700
of this pathway we just need to know the

377
00:14:19,430 --> 00:14:16,320
energy of this initial state and this

378
00:14:21,200 --> 00:14:19,440
final state but you could imagine that

379
00:14:23,300 --> 00:14:21,210
it's possible to have pathways where you

380
00:14:25,880 --> 00:14:23,310
first transfer an electron and then

381
00:14:28,600 --> 00:14:25,890
transfer a proton and this I will refer

382
00:14:31,700 --> 00:14:28,610
to as decoupled proton electron transfer

383
00:14:33,740 --> 00:14:31,710
now there's many many theories on this

384
00:14:36,320 --> 00:14:33,750
beautiful quantum mechanical theories

385
00:14:38,330 --> 00:14:36,330
but but I think the the real issue and

386
00:14:40,190 --> 00:14:38,340
understanding whether you have concerted

387
00:14:41,630 --> 00:14:40,200
proton electron transfer or whether you

388
00:14:44,300 --> 00:14:41,640

have this decoupled proton electron

389
00:14:47,150 --> 00:14:44,310
transfer just follows from very simple

390
00:14:48,830 --> 00:14:47,160
thermodynamic considerations and that

391
00:14:52,250 --> 00:14:48,840
just has to do with the stability of

392
00:14:54,770 --> 00:14:52,260
these four states typically if if these

393
00:14:55,970 --> 00:14:54,780
two states here are high in energy you

394
00:14:57,560 --> 00:14:55,980
could imagine that you will have

395
00:14:59,290 --> 00:14:57,570
concerted proton electron transfer

396
00:15:02,240 --> 00:14:59,300
simply because these two states are

397
00:15:07,520 --> 00:15:02,250
energetically unfavorable but once these

398
00:15:09,830 --> 00:15:07,530
states are favourable once this a likes

399
00:15:11,600 --> 00:15:09,840
to pick up an electron for instance

400
00:15:13,100 --> 00:15:11,610
because it has a favorable electron

401
00:15:15,140 --> 00:15:13,110
affinity and it has a good solvation

402
00:15:16,640 --> 00:15:15,150
energy then you could imagine that you

403
00:15:19,430 --> 00:15:16,650
first transfer an electron and then a

404
00:15:21,020 --> 00:15:19,440
proton and you can make things more

405
00:15:22,940 --> 00:15:21,030
complicated we can start transferring

406
00:15:24,670 --> 00:15:22,950
two protons and two electrons and we get

407
00:15:26,750 --> 00:15:24,680
these kind of square schemes and

408
00:15:28,400 --> 00:15:26,760
typically what people assume in the

409
00:15:32,090 --> 00:15:28,410
literature that things go along this

410
00:15:34,340 --> 00:15:32,100
diagonal but what I'll argue is that in

411
00:15:36,530 --> 00:15:34,350
many cases actually the mechanism follow

412
00:15:38,780 --> 00:15:36,540
something like this where we where

413
00:15:41,990 --> 00:15:38,790

somewhere in the mechanism we decouple

414
00:15:44,810 --> 00:15:42,000
proton electron transfer and we follow a

415
00:15:45,560 --> 00:15:44,820
pathway like this now how does that

416
00:15:49,100 --> 00:15:45,570
manifest

417
00:15:51,230 --> 00:15:49,110
in an experiment well if I apply again

418
00:15:54,139 --> 00:15:51,240
the subbatch a principle the idea that

419
00:15:56,689 --> 00:15:54,149
every every step here needs to be close

420
00:15:59,120 --> 00:15:56,699
to equilibrium in order to have the

421
00:16:00,439 --> 00:15:59,130
optimal rate and if I look at this step

422
00:16:02,840 --> 00:16:00,449
here this is just an acid-base

423
00:16:04,850 --> 00:16:02,850
equilibrium and if I want the acid-base

424
00:16:07,519 --> 00:16:04,860
equilibrium to be close to equilibrium

425
00:16:10,460 --> 00:16:07,529
that basically means that I want the pH

426
00:16:13,400 --> 00:16:10,470
of my solution to be close to the pKa of

427
00:16:15,800 --> 00:16:13,410
this acid-base equilibrium now that

428
00:16:17,480 --> 00:16:15,810
suggests that when you have decoupled

429
00:16:19,730 --> 00:16:17,490
proton electron transfer in your

430
00:16:22,100 --> 00:16:19,740
mechanism there's going to be an optimal

431
00:16:25,910 --> 00:16:22,110
pH at which the reaction likes to take

432
00:16:28,009 --> 00:16:25,920
place and this actually this very simple

433
00:16:30,259 --> 00:16:28,019
idea explains a lot of data in the

434
00:16:32,540 --> 00:16:30,269
electric Atallah C's literature so what

435
00:16:34,400 --> 00:16:32,550
I'm what I'm saying is that once I have

436
00:16:35,689 --> 00:16:34,410
this decoupled proton electron transfer

437
00:16:38,900 --> 00:16:35,699
in my mechanism there's going to be an

438
00:16:41,120 --> 00:16:38,910

optimal pH and so if I look at the rate

439
00:16:43,430 --> 00:16:41,130
at a fixed thermodynamic driving force I

440
00:16:45,499 --> 00:16:43,440
should say that this rate is at the same

441
00:16:46,970 --> 00:16:45,509
thermodynamic driving force for every pH

442
00:16:49,249 --> 00:16:46,980
it's very important to take that into

443
00:16:51,350 --> 00:16:49,259
account then there's going to be an

444
00:16:53,960 --> 00:16:51,360
optimal pH and that optimal pH is going

445
00:16:56,660 --> 00:16:53,970
to be very close to the pKa of the acid

446
00:16:58,790 --> 00:16:56,670
base equilibrium in the mechanism this

447
00:17:00,740 --> 00:16:58,800
explains why many alcohol oxidations

448
00:17:02,960 --> 00:17:00,750
prefer to take place in alkaline media

449
00:17:05,149 --> 00:17:02,970
because alcohols deep protonate an

450
00:17:07,970 --> 00:17:05,159
alkaline media to have a pKa of around

451
00:17:10,399 --> 00:17:07,980
14 or 15 and the deep protonated alcohol

452
00:17:13,730 --> 00:17:10,409
is more easy to oxidize than the

453
00:17:16,549 --> 00:17:13,740
protonated alcohol nitrate reduction

454
00:17:19,970 --> 00:17:16,559
prefers to take place in acid media

455
00:17:22,010 --> 00:17:19,980
nitrate has a pKa of minus 1 and

456
00:17:25,010 --> 00:17:22,020
actually prefers to be protonated before

457
00:17:27,020 --> 00:17:25,020
it reacts further and that's why nitrate

458
00:17:29,720 --> 00:17:27,030
prefers to have very to take place in

459
00:17:32,810 --> 00:17:29,730
very acidic media an intermediate case

460
00:17:35,180 --> 00:17:32,820
is formic acid oxidation formic acid has

461
00:17:36,649 --> 00:17:35,190
a pKa of 4 and we find that if we want

462
00:17:38,870 --> 00:17:36,659
to optimize the rate of formic acid

463
00:17:42,320 --> 00:17:38,880

oxidation for instance in a formic acid

464
00:17:45,530 --> 00:17:42,330
fuel cell the pH of the electrolyte

465
00:17:47,570 --> 00:17:45,540
should be close to 4 that doesn't

466
00:17:49,370 --> 00:17:47,580
necessarily optimize the conductivity of

467
00:17:53,390 --> 00:17:49,380
the electrolyte but it optimizes the

468
00:17:56,630 --> 00:17:53,400
rate of the of the catalytic reaction of

469
00:17:57,830 --> 00:17:56,640
the formic acid oxidation so what I want

470
00:17:59,270 --> 00:17:57,840
to do in the rest of the talk is show

471
00:18:00,890 --> 00:17:59,280
some of these principles in

472
00:18:03,920 --> 00:18:00,900
in relation to the electric analytics

473
00:18:05,540 --> 00:18:03,930
you to reduction if you look in the

474
00:18:07,400 --> 00:18:05,550
literature in purely the

475
00:18:11,690 --> 00:18:07,410
electrochemistry literature of co2

476
00:18:15,530 --> 00:18:11,700
reduction there's basically three major

477
00:18:17,840 --> 00:18:15,540
products that we observe Co formic acid

478
00:18:20,240 --> 00:18:17,850
we've seen them already as the initial

479
00:18:22,520 --> 00:18:20,250
reduction products of co2 and oxalate

480
00:18:25,940 --> 00:18:22,530
oxalate is typically a product in a

481
00:18:27,830 --> 00:18:25,950
protic solvents and all these reactions

482
00:18:29,480 --> 00:18:27,840
are to electron transfer reactions which

483
00:18:33,590 --> 00:18:29,490
I think it's not a coincidence these are

484
00:18:35,180 --> 00:18:33,600
relatively easy to catalyze and and

485
00:18:37,340 --> 00:18:35,190
actually there are catalysts that

486
00:18:39,290 --> 00:18:37,350
catalyze these reactions reversibly I'll

487
00:18:41,450 --> 00:18:39,300
show you an example in the next slide

488
00:18:43,850 --> 00:18:41,460

enzymes there exist enzymes that can

489
00:18:45,170 --> 00:18:43,860
catalyze these reactions reversibly so

490
00:18:48,020 --> 00:18:45,180
they can catalyze them in both

491
00:18:50,660 --> 00:18:48,030
directions with essentially zero zero

492
00:18:52,400 --> 00:18:50,670
over potential if you want to reduce

493
00:18:54,080 --> 00:18:52,410
them further then these are the

494
00:18:56,810 --> 00:18:54,090
intermediate so you can reduce co

495
00:18:58,400 --> 00:18:56,820
further to methane ethylene and other

496
00:18:59,720 --> 00:18:58,410
interesting products will copper

497
00:19:01,850 --> 00:18:59,730
electrodes I'll show you that in a

498
00:19:04,270 --> 00:19:01,860
minute and you can also imagine that you

499
00:19:06,140 --> 00:19:04,280
you oxidize further this carboxylate

500
00:19:10,400 --> 00:19:06,150
functionalities to an aldehyde and

501
00:19:12,500 --> 00:19:10,410
eventually to to an alcohol now just to

502
00:19:14,870 --> 00:19:12,510
show you that you can do this reversibly

503
00:19:17,330 --> 00:19:14,880
so you can reversibly convert co2 into

504
00:19:18,950 --> 00:19:17,340
formic acid in this case and back here's

505
00:19:22,430 --> 00:19:18,960
an example of an experiment from the

506
00:19:24,170 --> 00:19:22,440
group of Judy Hurst in Cambridge where

507
00:19:26,420 --> 00:19:24,180
they immobilize the formate

508
00:19:30,260 --> 00:19:26,430
dehydrogenase on the paralytic graphite

509
00:19:33,410 --> 00:19:30,270
electrode and and they basically they

510
00:19:36,980 --> 00:19:33,420
they change the potential at which the

511
00:19:40,100 --> 00:19:36,990
electrons are transferred to the active

512
00:19:42,860 --> 00:19:40,110
site in in this kind of protein film

513
00:19:45,140 --> 00:19:42,870

voltammetry here's the the redox

514
00:19:47,870 --> 00:19:45,150
potential of the conversion of form a to

515
00:19:50,120 --> 00:19:47,880
co2 if you go negative you see that you

516
00:19:51,830 --> 00:19:50,130
reduce co2 to formate and if you go back

517
00:19:54,020 --> 00:19:51,840
you see that you oxidize formate back

518
00:19:56,300 --> 00:19:54,030
into co2 and note that this happens

519
00:19:59,000 --> 00:19:56,310
essentially reversibly around the

520
00:20:00,680 --> 00:19:59,010
equilibrium potential showing that this

521
00:20:02,600 --> 00:20:00,690
two electron transfer reduction with the

522
00:20:04,700 --> 00:20:02,610
right catalyst these two electron

523
00:20:08,780 --> 00:20:04,710
transfer reaction can be catalyzed

524
00:20:10,880 --> 00:20:08,790
reversibly and and and this inspired me

525
00:20:13,220 --> 00:20:10,890
to see if we can also do this with

526
00:20:15,830 --> 00:20:13,230
something that is not an enzyme

527
00:20:19,279 --> 00:20:15,840
and and this comes the closest to what

528
00:20:21,700 --> 00:20:19,289
we find so far this is the the reduction

529
00:20:23,899 --> 00:20:21,710
of co2 on the platinum palladium

530
00:20:24,980 --> 00:20:23,909
catalyst and basically what we did

531
00:20:26,720 --> 00:20:24,990
there's a lot of literature

532
00:20:29,120 --> 00:20:26,730
electrochemistry literature on formic

533
00:20:31,009 --> 00:20:29,130
acid oxidation and the best catalyst

534
00:20:32,840 --> 00:20:31,019
that people found was a mixture of

535
00:20:35,419 --> 00:20:32,850
palladium and platinum we just took that

536
00:20:37,490 --> 00:20:35,429
catalyst and we ran it in Reverse and we

537
00:20:39,590 --> 00:20:37,500
found that we can reduce u2 to formate

538
00:20:41,629 --> 00:20:39,600

with this catalyst and we can do this

539
00:20:42,799 --> 00:20:41,639
you know almost quasi reversibly and you

540
00:20:44,539 --> 00:20:42,809
can see that very close to the

541
00:20:47,690 --> 00:20:44,549
equilibrium potential you start

542
00:20:50,029 --> 00:20:47,700
generating for me this is not a very

543
00:20:52,190 --> 00:20:50,039
stable catalyst it generates also co and

544
00:20:54,860 --> 00:20:52,200
co will poison the electrode but but

545
00:20:59,690 --> 00:20:54,870
this is just to to illustrate the

546
00:21:01,759 --> 00:20:59,700
principle here's another example when of

547
00:21:04,220 --> 00:21:01,769
a system that we studied this is a

548
00:21:06,259 --> 00:21:04,230
cobalt porphyrin or protoporphyrin that

549
00:21:08,330 --> 00:21:06,269
we immobilized on a graphite electrode

550
00:21:10,460 --> 00:21:08,340
we actually initially we were interested

551
00:21:12,620 --> 00:21:10,470
also in using this this catalyst for

552
00:21:14,389 --> 00:21:12,630
nitrate reduction but at some point we

553
00:21:17,240 --> 00:21:14,399
decided to see if this could be active

554
00:21:19,100 --> 00:21:17,250
for co2 reduction we follow this system

555
00:21:20,870 --> 00:21:19,110
with an online mass spectrometer here

556
00:21:22,789 --> 00:21:20,880
you see the negative current flowing as

557
00:21:25,519 --> 00:21:22,799
we make the potential more negative and

558
00:21:27,139 --> 00:21:25,529
actually I was I was expecting to see Co

559
00:21:29,899 --> 00:21:27,149
because this system had been studied

560
00:21:31,730 --> 00:21:29,909
already and it was found to make Co but

561
00:21:33,860 --> 00:21:31,740
we find actually that this specific

562
00:21:37,789 --> 00:21:33,870
system can make methane so it can do an

563
00:21:40,700 --> 00:21:37,799

8 electron transfer reaction from co2 to

564
00:21:43,399 --> 00:21:40,710
methane the the selectivity however is

565
00:21:46,129 --> 00:21:43,409
not heartwarming this is about 1% and

566
00:21:48,049 --> 00:21:46,139
99% is hydrogen because all this is

567
00:21:51,230 --> 00:21:48,059
taking place in water and water is also

568
00:21:53,629 --> 00:21:51,240
reduced by this catalyst to form

569
00:21:55,639 --> 00:21:53,639
hydrogen but but the interesting thing

570
00:21:59,029 --> 00:21:55,649
here is that this reaction is extremely

571
00:22:02,149 --> 00:21:59,039
sensitive to pH if we shift from pH 1 to

572
00:22:04,340 --> 00:22:02,159
pH 3 we see that we shift the formation

573
00:22:07,009 --> 00:22:04,350
of hydrogen to more negative potentials

574
00:22:09,529 --> 00:22:07,019
but the reduction of co2 still takes

575
00:22:11,450 --> 00:22:09,539
place at the same potential and we

576
00:22:13,279 --> 00:22:11,460
generate here we generate methane and

577
00:22:16,070 --> 00:22:13,289
now we can also see the formation of CO

578
00:22:18,860 --> 00:22:16,080
in our mass spectrometer and now we find

579
00:22:22,250 --> 00:22:18,870
that the formation of of CO at pH 3 can

580
00:22:24,980 --> 00:22:22,260
reach selectivities up to 60% and that

581
00:22:26,630 --> 00:22:24,990
of hydrogen ISM is much lower now

582
00:22:29,990 --> 00:22:26,640
there's different ways of look

583
00:22:33,350 --> 00:22:30,000
this but but the key reason why I think

584
00:22:35,510 --> 00:22:33,360
that this is so sensitive to pH is that

585
00:22:37,190 --> 00:22:35,520
the hydrogen evolution reaction is a

586
00:22:39,350 --> 00:22:37,200
reaction that takes place through

587
00:22:42,620 --> 00:22:39,360
concerted proton electron transfer and

588
00:22:44,900 --> 00:22:42,630

is not very sensitive to pH but the co2

589
00:22:47,390 --> 00:22:44,910
activation is a process that takes place

590
00:22:49,250 --> 00:22:47,400
through an initial electron transfer so

591
00:22:51,440 --> 00:22:49,260
we start from the cobalt porphyrin here

592
00:22:54,350 --> 00:22:51,450
if we reduce that from the 2 plus to the

593
00:22:56,570 --> 00:22:54,360
1 plus state that is when the co2 binds

594
00:22:58,160 --> 00:22:56,580
to the cobalt Center and this is just an

595
00:23:00,350 --> 00:22:58,170
electron transfer and the protons are

596
00:23:02,960 --> 00:23:00,360
only transferred later so here we

597
00:23:04,640 --> 00:23:02,970
decouple proton from electron transfer

598
00:23:06,920 --> 00:23:04,650
and that makes this cycle ph-sensitive

599
00:23:09,830 --> 00:23:06,930
and this cycle not and so now by playing

600
00:23:11,480 --> 00:23:09,840
with pH we can optimize not only

601
00:23:14,150 --> 00:23:11,490
activity but we can also optimize

602
00:23:18,380 --> 00:23:14,160
selectivity and we can tune the pathway

603
00:23:20,270 --> 00:23:18,390
that we want to take place now we've

604
00:23:22,910 --> 00:23:20,280
also studied we can actually calculate

605
00:23:25,040 --> 00:23:22,920
this I don't really want to dwell on

606
00:23:27,080 --> 00:23:25,050
this very much we actually played with

607
00:23:29,420 --> 00:23:27,090
the metal center of these porphyrins to

608
00:23:31,670 --> 00:23:29,430
see if that has an effect on the product

609
00:23:34,340 --> 00:23:31,680
that we make and we find that that

610
00:23:39,170 --> 00:23:34,350
typically our iron and cobalt tend to

611
00:23:41,750 --> 00:23:39,180
make CO and we find that rhodium indium

612
00:23:44,180 --> 00:23:41,760
and tin interestingly make formate they

613
00:23:46,550 --> 00:23:44,190

make a completely different product and

614
00:23:49,070 --> 00:23:46,560
we wanted to understand what property of

615
00:23:52,460 --> 00:23:49,080
the catalyst it is that that that

616
00:23:55,010 --> 00:23:52,470
determines this this selectivity and the

617
00:23:57,440 --> 00:23:55,020
classical theory in this area is that

618
00:23:59,240 --> 00:23:57,450
that has to do with the way you make the

619
00:24:01,910 --> 00:23:59,250
first intermediate and how that first

620
00:24:03,950 --> 00:24:01,920
intermediate binds to the catalyst if

621
00:24:06,380 --> 00:24:03,960
you bind that first intermediate through

622
00:24:08,390 --> 00:24:06,390
the carbon so you have a proton coupled

623
00:24:11,000 --> 00:24:08,400
electron transfer to the co2 and you

624
00:24:13,340 --> 00:24:11,010
make this COOH intermediate that binds

625
00:24:15,200 --> 00:24:13,350
through the carbon that in a next step

626
00:24:18,100 --> 00:24:15,210
you will break a co bond and you will

627
00:24:20,300 --> 00:24:18,110
end up with Co but if you if you

628
00:24:23,210 --> 00:24:20,310
transfer that first proton electron

629
00:24:25,970 --> 00:24:23,220
transfer to the carbon here and you bind

630
00:24:27,620 --> 00:24:25,980
through the oxygen then you make a kind

631
00:24:29,690 --> 00:24:27,630
of formate intermediate and this will

632
00:24:31,910 --> 00:24:29,700
dissociate from the catalyst and your

633
00:24:34,310 --> 00:24:31,920
product will be formic acid and all this

634
00:24:36,800 --> 00:24:34,320
is always in competition with hydrogen

635
00:24:38,990 --> 00:24:36,810
evolution and this is something again

636
00:24:40,280 --> 00:24:39,000
that you can calculate you can do DFT

637
00:24:41,570 --> 00:24:40,290
calculations for all your

638
00:24:43,820 --> 00:24:41,580

catalyst and you can see which

639
00:24:47,150 --> 00:24:43,830
intermediate binds the strongest or is

640
00:24:48,860 --> 00:24:47,160
binding the most favorable to the

641
00:24:51,530 --> 00:24:48,870
catalyst and in that way you can predict

642
00:24:54,080 --> 00:24:51,540
what kind of product you will you will

643
00:24:57,800 --> 00:24:54,090
make using using quantum chemical

644
00:25:01,190 --> 00:24:57,810
calculation now this did not allow us to

645
00:25:02,720 --> 00:25:01,200
explain our data on the on the different

646
00:25:05,240 --> 00:25:02,730
porphyrins and so we came up with a

647
00:25:09,050 --> 00:25:05,250
different mechanism we actually found

648
00:25:11,000 --> 00:25:09,060
that if we do this on indium or tin co2

649
00:25:13,940 --> 00:25:11,010
does not want to bind to the metal

650
00:25:16,460 --> 00:25:13,950
center and we also find that we do not

651
00:25:21,410 --> 00:25:16,470
reduce the metal center of indium and

652
00:25:24,020 --> 00:25:21,420
tin porphyrins what we reduce is the the

653
00:25:26,810 --> 00:25:24,030
ligand and we generate a hydrogen or

654
00:25:29,420 --> 00:25:26,820
actually we generate a hydride on the

655
00:25:34,640 --> 00:25:29,430
ligand we generate an h- on the ligand

656
00:25:38,750 --> 00:25:34,650
and this h- attacks the carbon of the co

657
00:25:41,120 --> 00:25:38,760
2 and this generates the formate and we

658
00:25:43,730 --> 00:25:41,130
find that we can generate that h- that

659
00:25:47,410 --> 00:25:43,740
hydride intermediate not only on the

660
00:25:50,090 --> 00:25:47,420
ligand we find it on indium and and tin

661
00:25:52,430 --> 00:25:50,100
protoporphyrin s-- we make it on the

662
00:25:55,730 --> 00:25:52,440
ligand on rhodium actually find we can

663
00:25:58,370 --> 00:25:55,740

make it on the metal center and serve

664
00:26:00,320 --> 00:25:58,380
rhodium is activated not by binding co2

665
00:26:02,420 --> 00:26:00,330
but rhodium is activated by binding a

666
00:26:05,570 --> 00:26:02,430
hydride and this hydride attacks than

667
00:26:10,300 --> 00:26:05,580
the co2 and that is the way in which you

668
00:26:12,890 --> 00:26:10,310
make formate so our idea of how how the

669
00:26:14,300 --> 00:26:12,900
selectivity of this reaction is is is

670
00:26:16,370 --> 00:26:14,310
determined is a little bit different

671
00:26:18,650 --> 00:26:16,380
from the some of the ideas that exist in

672
00:26:20,030 --> 00:26:18,660
the literature and we think it is it is

673
00:26:22,430 --> 00:26:20,040
really the nature of this nucleophilic

674
00:26:24,320 --> 00:26:22,440
attack that you have after you've

675
00:26:26,870 --> 00:26:24,330
reduced the catalyst that determines the

676
00:26:28,820 --> 00:26:26,880
product that you make if the if the

677
00:26:30,380 --> 00:26:28,830
electron density is located on the metal

678
00:26:32,540 --> 00:26:30,390
center you will bind through the carbon

679
00:26:35,090 --> 00:26:32,550
and you will make co if the electron

680
00:26:37,130 --> 00:26:35,100
density generates a hydride intermediate

681
00:26:41,870 --> 00:26:37,140
that hydride will attack the carbon and

682
00:26:43,670 --> 00:26:41,880
you will make you will make formate now

683
00:26:45,680 --> 00:26:43,680
we can reduce these products further and

684
00:26:47,900 --> 00:26:45,690
one metal that is very good in that is

685
00:26:50,150 --> 00:26:47,910
is copper and this was actually this was

686
00:26:52,640 --> 00:26:50,160
discovered in Japan or so far from here

687
00:26:53,850 --> 00:26:52,650
in the university of chiba by Yoshio

688
00:26:56,400 --> 00:26:53,860

hoary about 30

689
00:26:58,260 --> 00:26:56,410
years ago and he discovered that copper

690
00:27:03,120 --> 00:26:58,270
electrodes room-temperature aqueous

691
00:27:05,280 --> 00:27:03,130
media are able to reduce co2 and co2 now

692
00:27:07,080 --> 00:27:05,290
what I would call a non-trivial products

693
00:27:09,299 --> 00:27:07,090
like methane and especially ethylene

694
00:27:11,240 --> 00:27:09,309
here and also ethanol is interesting so

695
00:27:13,770 --> 00:27:11,250
we make a carbon-carbon bond

696
00:27:16,590 --> 00:27:13,780
electrochemically on copper electrodes

697
00:27:18,720 --> 00:27:16,600
and we studied this again with an online

698
00:27:20,549 --> 00:27:18,730
mass spectrometry system so here we can

699
00:27:22,919 --> 00:27:20,559
follow the formation of the gaseous

700
00:27:24,930 --> 00:27:22,929
product have we changed the potential so

701
00:27:27,750 --> 00:27:24,940
again here we start from zero volt we go

702
00:27:29,669 --> 00:27:27,760
more negative so we make the the

703
00:27:31,380 --> 00:27:29,679
environment more reductive and you see

704
00:27:33,900 --> 00:27:31,390
the current flowing year this is by the

705
00:27:36,030 --> 00:27:33,910
way mainly hydrogen formation as you can

706
00:27:38,460 --> 00:27:36,040
see here you see that as we go more

707
00:27:40,230 --> 00:27:38,470
negative from co2 we make some formic

708
00:27:42,780 --> 00:27:40,240
acid but formic acid is not reduced

709
00:27:46,260 --> 00:27:42,790
further on copper but what you can also

710
00:27:48,620 --> 00:27:46,270
see is that both from CO 2 and co we

711
00:27:50,880 --> 00:27:48,630
make methane and we make ethylene and

712
00:27:53,340 --> 00:27:50,890
you can see that these look very very

713
00:27:55,799 --> 00:27:53,350

similar these profiles that we measure

714
00:27:58,380 --> 00:27:55,809
in the mass spectrometer suggesting that

715
00:28:00,960 --> 00:27:58,390
CEO is an intermediate in the co2

716
00:28:03,570 --> 00:28:00,970
reduction so we go from co2 to CO and

717
00:28:06,780 --> 00:28:03,580
then we reduce a co further to methane

718
00:28:09,000 --> 00:28:06,790
and ethylene and especially the

719
00:28:10,980 --> 00:28:09,010
formation of ethylene is intriguing so

720
00:28:13,110 --> 00:28:10,990
how is this carbon-carbon bond made and

721
00:28:14,760 --> 00:28:13,120
we studied this on this the same

722
00:28:17,039 --> 00:28:14,770
reaction on single crystal so now we

723
00:28:19,560 --> 00:28:17,049
play with the structure of the copper

724
00:28:22,140 --> 00:28:19,570
catalyst here we start from Co because

725
00:28:24,060 --> 00:28:22,150
that allows us to to start playing with

726
00:28:26,700 --> 00:28:24,070
pH a little bit more than when we would

727
00:28:28,440 --> 00:28:26,710
we would use co2 because co2 itself is

728
00:28:31,919 --> 00:28:28,450
is involved in all kinds of pH dependent

729
00:28:34,110 --> 00:28:31,929
equilibria if we do this reaction of

730
00:28:36,090 --> 00:28:34,120
copper 1 1 1 so where the surface atoms

731
00:28:38,280 --> 00:28:36,100
are arranged in this exact "'l fashion

732
00:28:39,539 --> 00:28:38,290
you can see that we make methane and we

733
00:28:41,159 --> 00:28:39,549
make ethylene or you can see the

734
00:28:42,380 --> 00:28:41,169
profiles in the mass spectrum are very

735
00:28:44,669 --> 00:28:42,390
very similar

736
00:28:47,640 --> 00:28:44,679
suggesting that they they are made in

737
00:28:49,890 --> 00:28:47,650
the same pathway if we do the same

738
00:28:51,330 --> 00:28:49,900

reaction but now on copper 100 you know

739
00:28:52,530 --> 00:28:51,340
the atoms are arranged in a square

740
00:28:55,020 --> 00:28:52,540
fashion you see that you have a

741
00:28:58,010 --> 00:28:55,030
potential window where we only make

742
00:29:00,690 --> 00:28:58,020
ethylene but we make no methane

743
00:29:02,299 --> 00:29:00,700
apparently here the carbon-carbon bond

744
00:29:04,950 --> 00:29:02,309
formation happens first

745
00:29:08,399 --> 00:29:04,960
even though thermodynamically speaking

746
00:29:10,419 --> 00:29:08,409
the most favorable product is methane

747
00:29:12,820 --> 00:29:10,429
apparently this carbon-carbon bond

748
00:29:14,739 --> 00:29:12,830
formation is extremely sensitive to the

749
00:29:17,139 --> 00:29:14,749
structure of the surface it is also

750
00:29:21,009 --> 00:29:17,149
extremely sensitive to pH note that here

751
00:29:22,899 --> 00:29:21,019
I compare pH 7 and pH 13 if I go from pH

752
00:29:24,460 --> 00:29:22,909
7 to 13 note that the formation of

753
00:29:27,009 --> 00:29:24,470
ethylene shifts to less negative

754
00:29:28,629 --> 00:29:27,019
potential so it happens earlier whereas

755
00:29:30,789 --> 00:29:28,639
the formation of hydrogen still happens

756
00:29:32,979 --> 00:29:30,799
at the same potential so parently by

757
00:29:35,430 --> 00:29:32,989
playing with pH again I can play with

758
00:29:37,749 --> 00:29:35,440
the selectivity of the reaction and

759
00:29:39,789 --> 00:29:37,759
again I think this is because the

760
00:29:42,310 --> 00:29:39,799
formation of ethylene happens through a

761
00:29:44,409 --> 00:29:42,320
decoupled proton electron transfer that

762
00:29:46,869 --> 00:29:44,419
favors this reaction in very alkaline

763
00:29:48,789 --> 00:29:46,879

media the more alkaline the better and

764
00:29:52,389 --> 00:29:48,799
the higher the selectivity towards

765
00:29:53,979 --> 00:29:52,399
towards ethylene but to quickly take you

766
00:29:56,379 --> 00:29:53,989
through the mechanism that we think is

767
00:29:59,229 --> 00:29:56,389
happening so we start from co2 we make

768
00:30:02,139 --> 00:29:59,239
formic acid but that is not reduced any

769
00:30:03,849 --> 00:30:02,149
further we make co that binds to the

770
00:30:05,200 --> 00:30:03,859
catalyst and the reason why copper is

771
00:30:08,139 --> 00:30:05,210
such a good catalyst under these

772
00:30:11,229 --> 00:30:08,149
conditions for co2 reduction is that it

773
00:30:13,690 --> 00:30:11,239
is the only metal that binds co with an

774
00:30:15,820 --> 00:30:13,700
intermediate binding strength all other

775
00:30:17,859 --> 00:30:15,830
matters metals either bind it to weakly

776
00:30:20,440 --> 00:30:17,869
or bind it so strongly that they become

777
00:30:23,560 --> 00:30:20,450
poisoned for instance platinum can

778
00:30:25,029 --> 00:30:23,570
reduce co2 to co but co binds so

779
00:30:28,119 --> 00:30:25,039
strongly to platinum that it cannot

780
00:30:29,830 --> 00:30:28,129
reduce it any further this co can be

781
00:30:31,869 --> 00:30:29,840
further hydrogenated you make these type

782
00:30:33,339 --> 00:30:31,879
of intermediates the co bond will break

783
00:30:35,440 --> 00:30:33,349
at some point you will end up with

784
00:30:38,469 --> 00:30:35,450
methane some of these intermediates may

785
00:30:40,659 --> 00:30:38,479
dimerize and form ethylene and this is

786
00:30:42,580 --> 00:30:40,669
the pathway that happens on on copper

787
00:30:44,019 --> 00:30:42,590
one one one and and the rate determining

788
00:30:46,029 --> 00:30:44,029

step here is a conservative proton

789
00:30:49,269 --> 00:30:46,039
electron transfer but a couple 100

790
00:30:51,519 --> 00:30:49,279
something else happens remember that

791
00:30:54,249 --> 00:30:51,529
there we make only c2 and we don't make

792
00:30:56,769 --> 00:30:54,259
any c1 products at least in a certain

793
00:30:57,879 --> 00:30:56,779
potential window and the way we explain

794
00:31:00,129 --> 00:30:57,889
this is through this dimerization

795
00:31:02,229 --> 00:31:00,139
mechanism so we make a negatively

796
00:31:05,440 --> 00:31:02,239
charged dimer that binds to the surface

797
00:31:07,269 --> 00:31:05,450
and this negatively charged dimer is the

798
00:31:10,769 --> 00:31:07,279
key intermediate and that isn't further

799
00:31:13,570 --> 00:31:10,779
hydrogenated and this is made through a

800
00:31:16,509 --> 00:31:13,580
electron transfer step that is decoupled

801
00:31:19,570 --> 00:31:16,519
from proton transfer and this eventually

802
00:31:20,820 --> 00:31:19,580
ends up in ethylene but it can also

803
00:31:23,159 --> 00:31:20,830
generate as

804
00:31:25,769 --> 00:31:23,169
in a bifurcation that happened somewhere

805
00:31:27,860 --> 00:31:25,779
here later on in the pathway so what we

806
00:31:30,720 --> 00:31:27,870
happened what happens here is a kind of

807
00:31:33,269 --> 00:31:30,730
reductive dimerization or reductive Co

808
00:31:35,130 --> 00:31:33,279
coupling my organic chemistry colleagues

809
00:31:38,820 --> 00:31:35,140
tell me this is very similar to McMurray

810
00:31:40,440 --> 00:31:38,830
coupling there's various arguments that

811
00:31:42,360 --> 00:31:40,450
I can give why I think this is a

812
00:31:44,639 --> 00:31:42,370
reasonable pathway one of them is that

813
00:31:46,380 --> 00:31:44,649

we've calculated this by dou Y of T

814
00:31:49,440 --> 00:31:46,390
calculations and we find that actually

815
00:31:51,419 --> 00:31:49,450
the in the absence of solvent I should

816
00:31:53,940 --> 00:31:51,429
say the most stable configuration of the

817
00:31:55,379 --> 00:31:53,950
dimer is like this and we indeed find

818
00:31:57,659 --> 00:31:55,389
that it's negatively charged so if you

819
00:31:58,980 --> 00:31:57,669
put this kind of dimer on a couple 100

820
00:32:00,360 --> 00:31:58,990
surface in a quantum chemical

821
00:32:02,430 --> 00:32:00,370
calculation you will find that there's

822
00:32:04,980 --> 00:32:02,440
an electron transfer flowing from the

823
00:32:07,379 --> 00:32:04,990
copper into the dimer and if you

824
00:32:08,700 --> 00:32:07,389
actually view ad solvent the structure

825
00:32:10,409 --> 00:32:08,710
looks a little bit different but it's

826
00:32:12,299 --> 00:32:10,419
still negatively charged and it actually

827
00:32:13,950 --> 00:32:12,309
stabilizes because it is negatively

828
00:32:17,310 --> 00:32:13,960
charged the solvent actually helps

829
00:32:18,870 --> 00:32:17,320
stabilizing discharged intermediate and

830
00:32:20,129 --> 00:32:18,880
and through that we come to the

831
00:32:22,409 --> 00:32:20,139
conclusion that this is a very

832
00:32:24,240 --> 00:32:22,419
reasonable pathway interesting leaders

833
00:32:26,490 --> 00:32:24,250
can also explain why it is so sensitive

834
00:32:28,259 --> 00:32:26,500
to the structure because to bind this

835
00:32:31,139 --> 00:32:28,269
intermediate to the structure we find

836
00:32:33,480 --> 00:32:31,149
that we need these kind of sites on the

837
00:32:35,700 --> 00:32:33,490
surface this dimer really likes to sit

838
00:32:37,680 --> 00:32:35,710

on these kinds of square sites it

839
00:32:39,210 --> 00:32:37,690
doesn't like it doesn't like to sit on

840
00:32:41,519 --> 00:32:39,220
the surface where we do not have these

841
00:32:43,470 --> 00:32:41,529
square sites and that explains why it is

842
00:32:48,799 --> 00:32:43,480
so sensitive to the structure of the

843
00:32:53,070 --> 00:32:51,450
many people when I show there's always

844
00:32:55,019 --> 00:32:53,080
ask me do you have any evidence for this

845
00:32:56,909 --> 00:32:55,029
intermediate because this is just in DFT

846
00:32:59,759 --> 00:32:56,919
calculations can you see it using

847
00:33:01,529 --> 00:32:59,769
spectroscopy maybe well maybe we do and

848
00:33:04,669 --> 00:33:01,539
these are some data that we generated

849
00:33:07,799 --> 00:33:04,679
using in situ infrared spectroscopy

850
00:33:10,649 --> 00:33:07,809
where we find that very close to the

851
00:33:13,919 --> 00:33:10,659
onset of ethylene formation on copper

852
00:33:15,960 --> 00:33:13,929
100 we we measured these infrared

853
00:33:18,180 --> 00:33:15,970
spectra and we see two Co bands one

854
00:33:20,580 --> 00:33:18,190
seems to be a single Co bond the other

855
00:33:22,350 --> 00:33:20,590
seems to be a double Co bond we only see

856
00:33:24,509 --> 00:33:22,360
this on couple 100 we never see this on

857
00:33:26,940 --> 00:33:24,519
couple one on one and when we try to

858
00:33:28,710 --> 00:33:26,950
assign these bands we find that it

859
00:33:31,320 --> 00:33:28,720
doesn't correspond to anything that we

860
00:33:34,350 --> 00:33:31,330
can measure and the only thing it seems

861
00:33:36,810 --> 00:33:34,360
to correspond to when we do DFT

862
00:33:39,480 --> 00:33:36,820
patience is this type of hydrogenated

863
00:33:41,850 --> 00:33:39,490

dimer here that has Co frequencies that

864
00:33:43,710 --> 00:33:41,860
are relatively close to what we measure

865
00:33:45,660 --> 00:33:43,720
experimentally so this may be considered

866
00:33:48,360 --> 00:33:45,670
as at least some kind of evidence for

867
00:33:52,100 --> 00:33:48,370
the formation of a key intermediate in

868
00:33:56,220 --> 00:33:52,110
the in the CC coupling on copper 100

869
00:33:58,350 --> 00:33:56,230
that this this seems a bit of like an

870
00:34:02,280 --> 00:33:58,360
odd mechanism is this this seal

871
00:34:03,930 --> 00:34:02,290
dimerization but interestingly nature

872
00:34:08,250 --> 00:34:03,940
there's something very very similar not

873
00:34:10,860 --> 00:34:08,260
with Co but with n o nitric oxide

874
00:34:15,900 --> 00:34:10,870
reductase is an enzyme that catalyzes

875
00:34:18,120 --> 00:34:15,910
the reduction of no.2 nitrous oxide and

876
00:34:20,280 --> 00:34:18,130
there are various mechanisms for this I

877
00:34:22,380 --> 00:34:20,290
am NOT up to date about the mechanism as

878
00:34:24,620 --> 00:34:22,390
you can see this is a very old paper but

879
00:34:27,930 --> 00:34:24,630
one of the suggestions in this paper is

880
00:34:30,240 --> 00:34:27,940
that this enzyme catalyzes the reduction

881
00:34:33,930 --> 00:34:30,250
of NL by the formation of this NL dimer

882
00:34:36,090 --> 00:34:33,940
and only after the formation of the a no

883
00:34:40,350 --> 00:34:36,100
dimer you break the NL bond and you end

884
00:34:42,060 --> 00:34:40,360
up with n 2o so again here Ana Rita

885
00:34:44,310 --> 00:34:42,070
taste seems to have developed a

886
00:34:46,410 --> 00:34:44,320
reductive dimerization pathway at these

887
00:34:48,030 --> 00:34:46,420
low temperatures to make NN bombs and

888
00:34:50,220 --> 00:34:48,040

what I'm suggesting is that for Co you

889
00:34:51,570 --> 00:34:50,230
can have something similar and the

890
00:34:53,340 --> 00:34:51,580
interesting experiment that we're trying

891
00:34:55,950 --> 00:34:53,350
to do now in my lab is to see if we use

892
00:34:59,190 --> 00:34:55,960
mixtures of CO and I know if we can make

893
00:35:00,900 --> 00:34:59,200
C as C n bones in this way so far the

894
00:35:03,450 --> 00:35:00,910
results have not been positive but we

895
00:35:07,860 --> 00:35:03,460
may have to tweak we have to tweak the

896
00:35:09,740 --> 00:35:07,870
the conditions a little bit a final

897
00:35:13,110 --> 00:35:09,750
thing that I wanted to show is that

898
00:35:14,700 --> 00:35:13,120
actually because these intermediates in

899
00:35:16,800 --> 00:35:14,710
these catalytic pathways are in this

900
00:35:18,840 --> 00:35:16,810
case negatively charged they are

901
00:35:21,390 --> 00:35:18,850
extremely sensitive to the nature of the

902
00:35:24,150 --> 00:35:21,400
electrolyte not only to the pH but also

903
00:35:26,100 --> 00:35:24,160
to the the cations that exists in the

904
00:35:28,440 --> 00:35:26,110
electrolyte and this was actually

905
00:35:32,280 --> 00:35:28,450
already observed by by by jaurim

906
00:35:34,770 --> 00:35:32,290
many years ago that the the selectivity

907
00:35:36,870 --> 00:35:34,780
to ethylene is very very sensitive to

908
00:35:38,660 --> 00:35:36,880
the nature of the cation in the

909
00:35:41,130 --> 00:35:38,670
electrolyte and we find that we see in

910
00:35:43,230 --> 00:35:41,140
an enhancement in the formation of

911
00:35:45,090 --> 00:35:43,240
ethylene when we do this in cesium

912
00:35:47,370 --> 00:35:45,100
hydroxide whereas in lithium hydroxide

913
00:35:50,190 --> 00:35:47,380

we see much less ethylene form

914
00:35:53,760 --> 00:35:50,200
and interestingly in cesium hydroxide we

915
00:35:55,800 --> 00:35:53,770
also start seeing c3 products again

916
00:35:58,560 --> 00:35:55,810
they're actually there's a bit of a

917
00:36:00,990 --> 00:35:58,570
debate in in the community right now how

918
00:36:02,790 --> 00:36:01,000
to explain this we have done some DFT

919
00:36:05,250 --> 00:36:02,800
calculations that suggest that the

920
00:36:07,470 --> 00:36:05,260
presence of cesium seems to have a

921
00:36:08,910 --> 00:36:07,480
positive effect on the stability of some

922
00:36:10,890 --> 00:36:08,920
of the intermediate so it acts like a

923
00:36:13,560 --> 00:36:10,900
kind of promoter it put a sort of

924
00:36:14,760 --> 00:36:13,570
flattens out the catalytic landscape but

925
00:36:17,910 --> 00:36:14,770
there are other other theories that

926
00:36:21,090 --> 00:36:17,920
suggest that that this has an effect on

927
00:36:25,110 --> 00:36:21,100
the local pH and that may have been an

928
00:36:27,270 --> 00:36:25,120
effect only on the final selectivity the

929
00:36:29,460 --> 00:36:27,280
formation of c3 is something that that

930
00:36:31,920 --> 00:36:29,470
is also interesting I think this happens

931
00:36:34,170 --> 00:36:31,930
through a kind of Co insertion mechanism

932
00:36:37,290 --> 00:36:34,180
it has been found that if you mix

933
00:36:38,820 --> 00:36:37,300
ethylene and co electrochemically and

934
00:36:41,160 --> 00:36:38,830
you reduce that electro chemically you

935
00:36:45,990 --> 00:36:41,170
you can make propionaldehyde and that

936
00:36:47,880 --> 00:36:46,000
can be reduced further to 2-propanol it

937
00:36:49,920 --> 00:36:47,890
looks like under these conditions again

938
00:36:52,590 --> 00:36:49,930

electrochemical conditions aqueous

939
00:36:54,480 --> 00:36:52,600
solutions we have some kind of electro

940
00:36:56,970 --> 00:36:54,490
hydroformylation reactions that can take

941
00:37:00,240 --> 00:36:56,980
place that allow us to grow these carbon

942
00:37:02,460 --> 00:37:00,250
chains the final thing is that when this

943
00:37:03,990 --> 00:37:02,470
takes place this always happens

944
00:37:06,360 --> 00:37:04,000
simultaneously with hydrogen evolution

945
00:37:08,640 --> 00:37:06,370
that means that locally the pH is

946
00:37:12,020 --> 00:37:08,650
increasing so any formaldehyde or

947
00:37:14,340 --> 00:37:12,030
aldehydes that we make will take part in

948
00:37:17,280 --> 00:37:14,350
disproportion asian reactions and we

949
00:37:20,130 --> 00:37:17,290
typically see that when we see alcohols

950
00:37:22,290 --> 00:37:20,140
we also see carboxylic acids so when we

951
00:37:24,240 --> 00:37:22,300
see ethanol we almost always also see

952
00:37:26,340 --> 00:37:24,250
acetate which suggests that actually

953
00:37:28,680 --> 00:37:26,350
what we make is a seed aldehyde that is

954
00:37:31,800 --> 00:37:28,690
disproportionate that disproportionate

955
00:37:35,430 --> 00:37:31,810
due to the low Heikal to do the high a

956
00:37:36,890 --> 00:37:35,440
local pH into the into the alcohol and

957
00:37:38,090 --> 00:37:36,900
the carboxylic acid or at or

958
00:37:40,470 --> 00:37:38,100
carboxylated

959
00:37:42,180 --> 00:37:40,480
okay that brings me to the final slide I

960
00:37:43,830 --> 00:37:42,190
showed you that it's possible to reduce

961
00:37:45,810 --> 00:37:43,840
you to close to the somewhat and I'm a

962
00:37:47,400 --> 00:37:45,820
potential but you should restrict

963
00:37:48,480 --> 00:37:47,410

yourself to two electron transfer and

964
00:37:50,250 --> 00:37:48,490
then you can find the optimal

965
00:37:52,550 --> 00:37:50,260
intermediate if you have the right

966
00:37:55,560 --> 00:37:52,560
catalyst we try to argue that the

967
00:37:57,150 --> 00:37:55,570
activation 2co of formic acid follows

968
00:38:00,120 --> 00:37:57,160
different pathways depending on the

969
00:38:01,230 --> 00:38:00,130
nature of the nucleophilic attack that

970
00:38:03,740 --> 00:38:01,240
under electrochemical

971
00:38:06,000 --> 00:38:03,750
we make these charged intermediates and

972
00:38:07,770 --> 00:38:06,010
that means that these reactions are very

973
00:38:09,000 --> 00:38:07,780
very sensitive to pH and they're

974
00:38:11,820 --> 00:38:09,010
sensitive to the nature of the

975
00:38:13,500 --> 00:38:11,830
electrolyte and specifically the kind of

976
00:38:15,390 --> 00:38:13,510
cations that you have in solution and

977
00:38:17,280 --> 00:38:15,400
that you have somewhat unusual

978
00:38:19,800 --> 00:38:17,290
carbon-carbon bond formation pathways

979
00:38:21,270 --> 00:38:19,810
like reductive dimerization and maybe

980
00:38:23,100 --> 00:38:21,280
electrolyte a formulation is not so

981
00:38:25,620 --> 00:38:23,110
unusual but it's not always considered

982
00:38:28,380 --> 00:38:25,630
in the mechanisms that people have

983
00:38:30,060 --> 00:38:28,390
suggested final slide these are the PhD

984
00:38:32,700 --> 00:38:30,070
students postdocs that were involved in

985
00:38:33,690 --> 00:38:32,710
this work and the funding agencies and I

986
00:38:45,660 --> 00:38:33,700
would like to thank you for your

987
00:38:48,480 --> 00:38:45,670
attention okay questions I don't know if

988
00:38:54,600 --> 00:38:48,490

I should throw it that far might bonk

989
00:38:59,760 --> 00:38:54,610
somebody in the head sorry just to ask

990
00:39:01,410 --> 00:38:59,770
the obvious question you made us aware

991
00:39:03,510 --> 00:39:01,420
that this is not your field but I would

992
00:39:06,300 --> 00:39:03,520
like to know what you think about the

993
00:39:07,830 --> 00:39:06,310
situation four billion years ago 4.2

994
00:39:09,990 --> 00:39:07,840
billion years ago when life was starting

995
00:39:12,270 --> 00:39:10,000
how do you see this happening so many of

996
00:39:14,310 --> 00:39:12,280
us would like to see co2 being fixed

997
00:39:16,860 --> 00:39:14,320
some people don't like it some people

998
00:39:18,420 --> 00:39:16,870
say molecules came from space and people

999
00:39:21,780 --> 00:39:18,430
say they did come from here but not from

1000
00:39:24,570 --> 00:39:21,790
co2 how do you see it so what would be

1001
00:39:26,400 --> 00:39:24,580
your point is for us in the those of us

1002
00:39:29,690 --> 00:39:26,410
trying to make molecules from zero from

1003
00:39:35,760 --> 00:39:34,050
Wow that's it I think this should be

1004
00:39:38,040 --> 00:39:35,770
considered that that's all I can say I

1005
00:39:42,350 --> 00:39:38,050
mean it's very difficult to to answer

1006
00:39:44,220 --> 00:39:42,360
that question I'm just pointing out that

1007
00:39:45,390 --> 00:39:44,230
there are many different types of

1008
00:39:47,130 --> 00:39:45,400
catalysts one of the things I was

1009
00:39:49,740 --> 00:39:47,140
thinking about this morning what if you

1010
00:39:51,330 --> 00:39:49,750
have small metal nanoparticles I mean

1011
00:39:54,570 --> 00:39:51,340
that could act as catalysts as wellness

1012
00:39:56,310 --> 00:39:54,580
is not just ions there are many

1013
00:39:58,830 --> 00:39:56,320

different pathways out there that that's

1014
00:40:00,480 --> 00:39:58,840
it I think my main idea and it's very

1015
00:40:01,980 --> 00:40:00,490
difficult to choose which ones would

1016
00:40:04,740 --> 00:40:01,990
have played a role maybe they've all

1017
00:40:06,360 --> 00:40:04,750
played a role somehow I think the key

1018
00:40:10,470 --> 00:40:06,370
really is how or how did all this

1019
00:40:16,599 --> 00:40:10,480
organize into something like a cell that

1020
00:40:22,220 --> 00:40:19,220
thank you very much great talk so I

1021
00:40:24,740 --> 00:40:22,230
think emergence of selectivity of

1022
00:40:26,750 --> 00:40:24,750
catalyst is a one of the key topics of

1023
00:40:29,620 --> 00:40:26,760
play by the chemistry and you clearly

1024
00:40:31,520 --> 00:40:29,630
demonstrated if we can control

1025
00:40:34,130 --> 00:40:31,530
decoupling and a coupling rhythm

1026
00:40:36,770 --> 00:40:34,140
transfer just change the pH we can

1027
00:40:39,320 --> 00:40:36,780
control selectivity at the point you

1028
00:40:41,450 --> 00:40:39,330
talk right in the first topics and my

1029
00:40:43,010 --> 00:40:41,460
question is I think selectivity depends

1030
00:40:44,570 --> 00:40:43,020
on many things it depends on having the

1031
00:40:46,970 --> 00:40:44,580
right catalyst but also having the right

1032
00:40:49,070 --> 00:40:46,980
catalytic conditions like pH but also

1033
00:40:50,570 --> 00:40:49,080
electrolyte what I'm trying to say I

1034
00:40:52,520 --> 00:40:50,580
guess is that the the issue of

1035
00:40:54,380 --> 00:40:52,530
selectivity is a very complex one and is

1036
00:40:56,420 --> 00:40:54,390
one that you can tune in many different

1037
00:40:58,400 --> 00:40:56,430
ways and we're not always considering

1038
00:41:01,430 --> 00:40:58,410

all these different ways okay so

1039
00:41:02,870 --> 00:41:01,440
question can you rationally predict so

1040
00:41:05,630 --> 00:41:02,880
it's about you have this kind of

1041
00:41:07,310 --> 00:41:05,640
material with that experiment can you

1042
00:41:11,210 --> 00:41:07,320
predict all this material have a

1043
00:41:13,280 --> 00:41:11,220
function to D capo or capo yes you can

1044
00:41:15,020 --> 00:41:13,290
predict if you if you know the pka's of

1045
00:41:16,670 --> 00:41:15,030
of the different intermediates involved

1046
00:41:19,310 --> 00:41:16,680
and then you can say which which one

1047
00:41:21,650 --> 00:41:19,320
should you should take place it's a

1048
00:41:26,900 --> 00:41:21,660
neutral pH conditions and which ones are

1049
00:41:29,480 --> 00:41:26,910
less likely as pathway hey thanks for

1050
00:41:31,460 --> 00:41:29,490
that some point you mentioned the

1051
00:41:33,140 --> 00:41:31,470
hydrogen evolution reaction and how it

1052
00:41:35,660 --> 00:41:33,150
generates pH gradients that create

1053
00:41:37,970 --> 00:41:35,670
localized alkaline environments one of

1054
00:41:39,620 --> 00:41:37,980
the key types of mechanisms in

1055
00:41:41,090 --> 00:41:39,630
biochemistry is the formation of an

1056
00:41:42,620 --> 00:41:41,100
enolate which then goes on to

1057
00:41:47,030 --> 00:41:42,630
carboxylate something which can form a

1058
00:41:48,770 --> 00:41:47,040
CC bond that way I'm wondering is it how

1059
00:41:50,960 --> 00:41:48,780
powerful is that or how fast is that

1060
00:41:52,940 --> 00:41:50,970
hydrogen release reaction have to be so

1061
00:41:55,599 --> 00:41:52,950
that you could build up a localized

1062
00:41:57,890 --> 00:41:55,609
alkaline environment strong enough to

1063
00:41:59,720 --> 00:41:57,900

form an enolate from a ketone for

1064
00:42:01,550 --> 00:41:59,730
instance is that feasible or is

1065
00:42:02,950 --> 00:42:01,560
diffusion so fast that you can never

1066
00:42:07,099 --> 00:42:02,960
form such a strongly alkaline

1067
00:42:08,300 --> 00:42:07,109
environment how can I answer that if I

1068
00:42:12,140 --> 00:42:08,310
don't know if you don't have a question

1069
00:42:13,880 --> 00:42:12,150
I would need to know the local current

1070
00:42:16,790 --> 00:42:13,890
density which is something that's not so

1071
00:42:18,500 --> 00:42:16,800
yeah but it really depends on the rate

1072
00:42:21,190 --> 00:42:18,510
with which we generate hydrogen and the

1073
00:42:23,930 --> 00:42:21,200
rate with which you can replenish the

1074
00:42:26,300 --> 00:42:23,940
proton donor and if those are

1075
00:42:27,410 --> 00:42:26,310
sufficiently different you will have pH

1076
00:42:32,509 --> 00:42:27,420
gradients

1077
00:42:34,430 --> 00:42:32,519
buffer capacity if the local buffer

1078
00:42:37,759 --> 00:42:34,440
capacity is poor then the pH gradient

1079
00:42:39,140 --> 00:42:37,769
will be will be bigger as well that's

1080
00:42:41,180 --> 00:42:39,150
another parameter actually buffer

1081
00:42:43,069 --> 00:42:41,190
capacity can have a huge influence here

1082
00:42:44,809 --> 00:42:43,079
on the selectivity of the reaction

1083
00:42:48,140 --> 00:42:44,819
simply by it by the fact that it

1084
00:42:50,509 --> 00:42:48,150
generates different pH gradients okay

1085
00:42:55,759 --> 00:42:50,519
one last question while relay get set up

1086
00:42:57,349 --> 00:42:55,769
for the next time mark let me say I

1087
00:42:59,180 --> 00:42:57,359
think there was the most rational talk

1088
00:43:00,920 --> 00:42:59,190

I've ever heard on this subject and it

1089
00:43:03,259 --> 00:43:00,930
is fantastic

1090
00:43:05,359 --> 00:43:03,269
what happens if you use let's say liquid

1091
00:43:07,700 --> 00:43:05,369
ammonia where you can actually inject an

1092
00:43:11,839 --> 00:43:07,710
electron and have it sit in the solution

1093
00:43:13,549 --> 00:43:11,849
or HM PA what do you see then actually

1094
00:43:16,370 --> 00:43:13,559
if you reduce the oh and liquid ammonia

1095
00:43:18,049 --> 00:43:16,380
you make a seal dimer that that is that

1096
00:43:20,390 --> 00:43:18,059
is one of the reasons why why I think

1097
00:43:23,059 --> 00:43:20,400
the seal dimer is or is a reasonable

1098
00:43:25,309 --> 00:43:23,069
intermediate what about you you avoid

1099
00:43:27,200 --> 00:43:25,319
you avoid a protonation reaction because

1100
00:43:30,309 --> 00:43:27,210
what about co2 can you make oxalate

1101
00:43:32,210 --> 00:43:30,319
dianna oxalate will be the product I

1102
00:43:34,309 --> 00:43:32,220
should have had your chat with a

1103
00:43:36,410 --> 00:43:34,319
graduate student who spent six months

1104
00:43:42,049 --> 00:43:36,420
spraying ammonia all over everything

1105
00:43:45,009 --> 00:43:42,059
trying that would solve the ammonia

1106
00:43:47,539 --> 00:43:45,019
problem though wouldn't it very good

1107
00:43:50,420 --> 00:43:47,549
okay so let's move on to the next talk

1108
00:43:52,160 --> 00:43:50,430
which will be given by actually let's

1109
00:43:55,400 --> 00:43:52,170
take mark again

1110
00:44:46,710 --> 00:43:55,410
[Applause]