CARNICOM INSTITUTE LEGACY PROJECT

A Release of Internal Original Research Documents

Authored
by
Clifford E Carnicom
President, Carnicom Institute

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Apr 2015 – May 2015

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3 SUBJECT

120 Sheets

COLLEGE RULED

Carnicom Institute
Notes

April 2015 ~~Feb 2013~~ –
May 2015

Apr 17 2015
We now Continue with CDB.
Now the spreadsheet is to the following.

We have a Carboxylic
Our range is 3600 - 2400.
Mid range is ~ 3000
IR Spec Range is 2500 - 3100. Enter it

Now Toolbox gives a range of 2500 - 3300
So notice the difference. This is important.
Avg = 3200 to start.

Now go to Pavia, Pavia gives 3400 - 2400
Now our average is 3267 - 2467
Koji is at 3200 - 2450

Looks to me like our most reasonable values are
3300 - 2450

* So let's use COOH @ 3300 - 2450
In the Future

This gave us a Pr value of 61%. This is very reasonable.

Page 2

Next we have 2 subpeaks
2900 C-H Alkane CH_2 methylene

~~2820~~ 2830 aldehyde

These have already been worked up.

Now as we look @ the further there is a significant slope change from

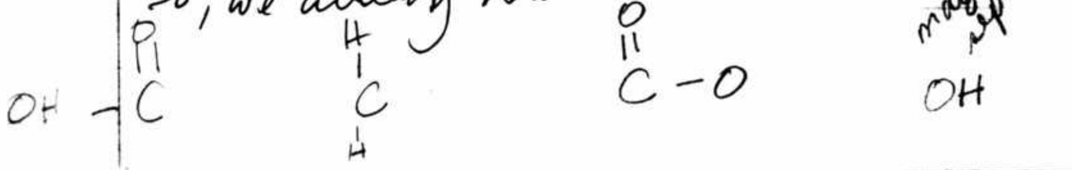
3600 - 3035 Something is happening here.
Toolbox? Our closest pick here is an alcohol.
Look @ Carboxylic reference graph.
Not really this Change.
But it looks to me a Combo of OH
& CH This make perfect sense.

So indeed this what we have. A Combination of an alcohol & C-H.

Toolbox OH is ~3550 - 3250
IR Spec is 3600 - 3200

Now we have additional modest activity @ 2640.
The range is about 50 on each side.
An aldehyde is our best option here.
This correlates.
IR Spec Aldehyde 2720 This is a modest correlation

So, we already have



$$OH-\overset{\overset{O}{\|}}{C} \qquad \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \qquad \overset{\overset{O}{\|}}{C}-O \qquad OH$$

maybe separate

[redacted]

Page 3

Our next peak @ 1700 practitioners
Carbonyl Straight as can be.

But alcohols do not have a carbonyl ?!!?
No, but carbonyls can exist separate from alcohols

Our Carbonyl is @ 1700 exactly
~~The range~~ Our range is 1600-1800
IR Spec 1670-1780

IR Spec - peak @ 1710 C=O saturated

Now we go to ~~1400~~ 1410
This was a very interesting case
We know that we have a combined influence of the alkane bends + unknown @ 1410.

Now look @ the compounding influence
Something right @ ~~1400~~. 1410

You only have alkane & nitro.
Nitro N-O aliphatic is our only choice to combine @ 1380 weak. IR Spec

but Koji gives us C=C-H
from 1400-1420
So this is ~~alkane~~ alkene
but IR spec & Toolbox do not show this.

Page 4

We have a very interesting case w/ Koji
@ 1410 (Koji, 1420)
He is citing a alkene bending motion
with the most likely term

$R-CH=CH_2$

he is also calling it a vinyl Table 2

In his correlation tables he cites
$C=C-H$ as the
We could just take this.

This is an interesting case

Now we have a strong peak @ 1210.
This is different also.

Now we have a range here of
1165 – 1310
This range fits an ester or a carboxylic acid.
This is tricky. IR spec

An ester says two bands. That does not bode well.
Actually we do have two bands 1720 & 1260 See Toolbox

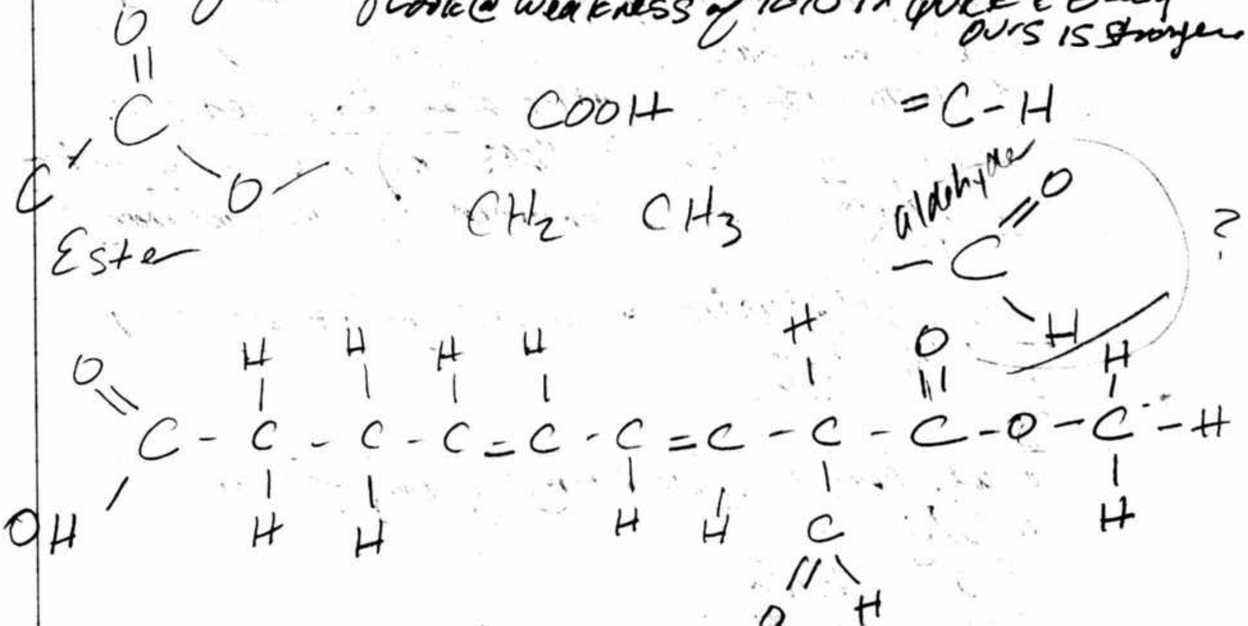
But toolbox gives an ideal range for this as
Esters 1180-1290.
asymmetrical — C-O-C stretch.

IR Spec also give a peak of 1260 Strong for an alkane, alkene ?.

We may have combined influence here.

I think @ 1260 that we have a combined influence of a COOH and an ester

look @ weakness of 1210 in Quick & Easy
ours is stronger



This is our proposed
CDB structure
Still need 920 & 715
(Kojic?)

Two new pens today. The one is not bad it seems. And then we try the other one. And it is a little better. If we move the holder or the first one it is much better.

Apr 19 2015 Page 6

Continuing w/ 920 & 715.

Now, on 920, we are making the case that this corresponds to a bending motion of R-CH=CH$_2$ (vinyl) in Table 2, #3.

For now, we have simplified this to that of the correlation chart C=C-H of 1400-1420. Notice also Koji lists a stretching C=C @ 1645 (m). Our question is ~~whether~~ this is combined w/ our carbonyl @ 1700

Notice the disturbance on our plot of COB lipids @ 1650.

So we have a few things going for us including
910 activity
1420 activity
and possible 1650 activity.
all of which support our selection of Koji of C=C-H in her correlation chart.
No one else, ie IRspec & Toolbox seem to include a know of this vibrational set.

Now the other point of ~~interest~~ here is the general form of

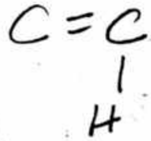
$C=C-H$

vs

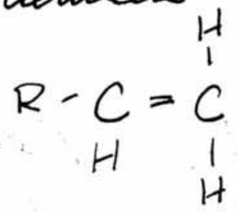
the more specific form of Koji @ this specific frequency set. And he is choosy.

$R-CH=CH_2$ He uses the word vinyl.

So the comparison is between

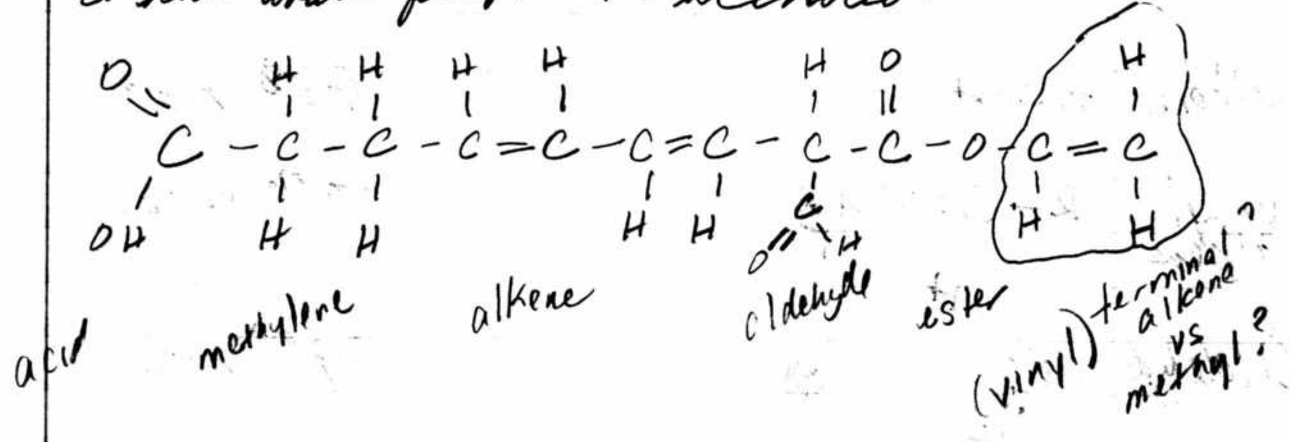


$\underset{\displaystyle H}{C=C}$

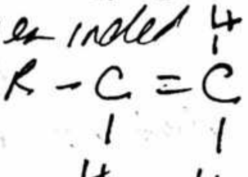


$R-\underset{\displaystyle H}{C}=\overset{\displaystyle H}{\underset{\displaystyle H}{C}}$

So then would propose the scenario:



The next question concerns 715.
But before, yes indeed



$R-\underset{\displaystyle H}{C}=\overset{\displaystyle H}{\underset{\displaystyle H}{C}}$

is the vinyl functional group.
The vinyl group is definitely subject to polymerization.

Page 8

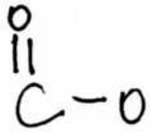
all peaks have now been

OK, we have finished the analysis on CDB liquids of low resolution spectra. We potentially have very significant findings.

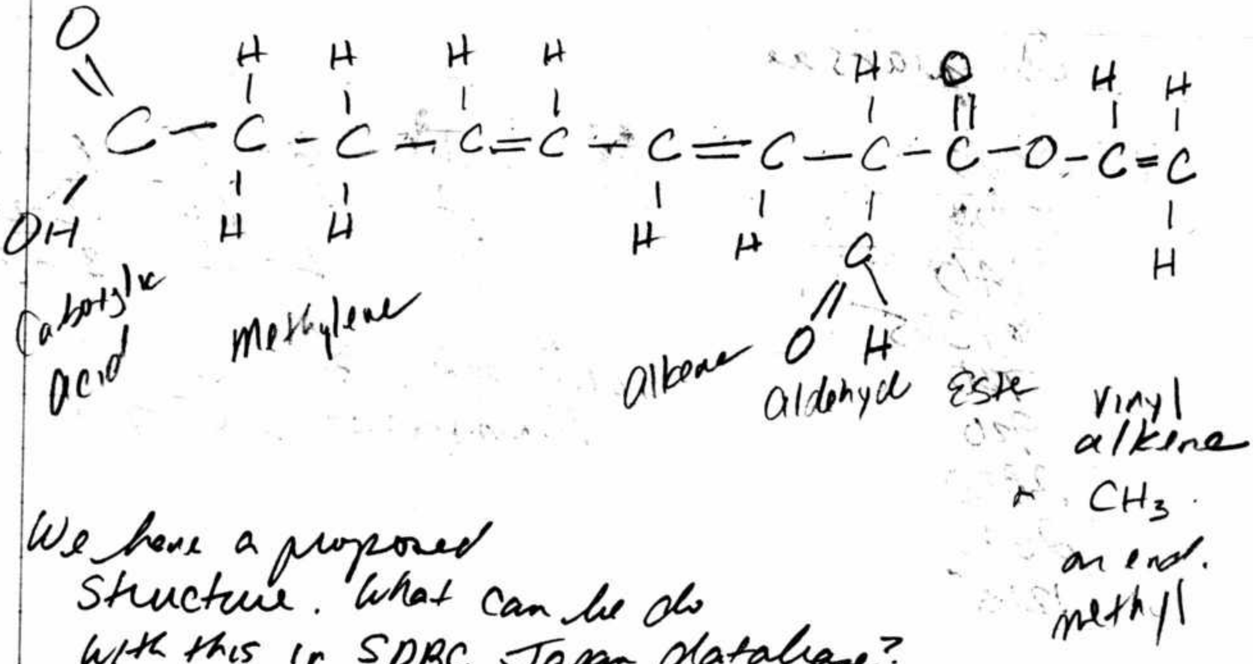
Our groups identified are:

	COOH		100%	n=3
alkane	CH CH_2	Methylene	91%	n=2
	CH_3	Methyl	89%	n=1
alkene	$=C-H$		65%	n=2
Vinyl alkene	$R-C=CH_2$		70%	n=2
Aldehyde			99%	n=2
General Alkene	$C=O$		100%	
Alcohol	OH		76%	n=1

No evidence beyond that of Carboxylic acid.

Ester	 $\overset{O}{\overset{\Vert}{C}}-O$	94%	n=2

We can, therefore, formulate a preliminary structure.



We have a proposed Structure. What can we do with this in SDBC Japan database?

Characteristics
1. Acid
2. Conjugation
3. Oxygenated
4. Halogen affinity
5. Double C=C bonds apparently subject to oxidation.
6. Vinyl functional group
7. Unsaturated
8. Combustible

Found in:
dental products
floor polish
paint
leather finishings
paper coatings
plastics
textiles

Page 10

1^ SDBS
our structure is $C_{12}H_{16}O_5$

Our peaks are

2900
1710
1440
~~to~~ 1365
720
920
2830
2640
1265

C	6 - 18	8 - 16
H	12 - 25	12 - 20
O	2 - 10	3 - 8

allowance ~~30~~ 20
Transmittance <~~85~~ 70

You can also tighten up on atom numbers instead of transmittance & allowance

Hits:
propionic acid

Allowance 20
Max T 60%

8 hits

hexadienoic acid
benzo thiophene-6 carboxylic acid - ~~forbidden~~?

Lipidomics Gateway Web Site

20,10 = 36 ethylene

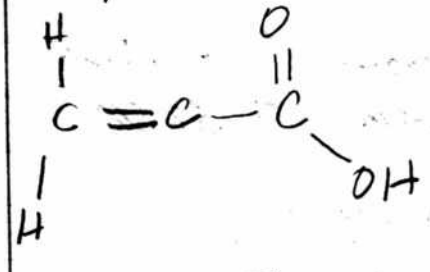
In Lipid database, hits for vinyl

Vinyl acetic acid] these look (butenoic acid)
Vinyl acrylic acid] like good tagets (pentadienoic acid)
looks also to be called acrylic acid

Main Class: Fatty acids & Conjugates
Sub Class: Unsaturated fatty acids

IUPAC name: Prop-2-enoic acid

Acrylic Acid Skeletal



other names:
acroleic acid
ethylenecarboxylic acid
propene acid
vinylformic acid

Esters appear to be associated w/ waxes
Esters exist within phospholipids
and triglycerides.

Fatty esters
Fatty aldehydes (can be toxic when heating polyunsaturated oils

Okay, lets move to Urine [redacted] Analyses
w/ spreadsheet.

First, we have a major peak near 3350.
These are above 3000. So we have either
unsaturated C-H or amines.
Notice the dramatic shift in slope.
We also appear to have a carbonyle.
The case for carboxylic ~~ac~~ acid is
already very strong. There is an important
slope break @ ~ 3080.

So I see our first peak range from about
3420 - 3080. Midpoint = 3250

Toolbox has amine 3460 - 3280.
Looks to be our best bet right now.
IR Spec:
Alcohol does not fit well

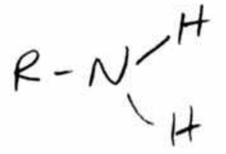
IRSpec gives amine from 4000 - 3000
Amine looks like the strongest Candidate.

Now look @ the subpeaks
~~3350~~ 3460 IR Spec gives amine (3300 - 3500)
Could be amide Toolbox 3440 - 3420
3340 Could be amide 3360 - 3340
→ 3400 - 3000 is amine, this is close Toolbox
3190 3200 - 3180 is Amide Toolbox

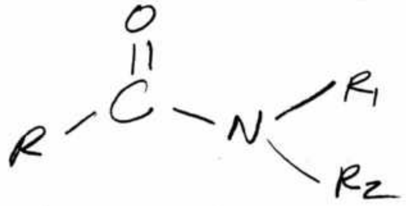
Not great yet

What is the difference between amine and amide?

Amine



Amide



We may have both @ this time.

Notice we actually have another slope break.

Our first peak is really a range from 3150 – 3460

Toolbox has 3280 – 3460 for Amine
We seem to have Combo of amide & amine.

Next, some kind of slope break.
3150 – 3080 / Midpoint = 3115
Toolbox best is an alkene (3020 – 3100)

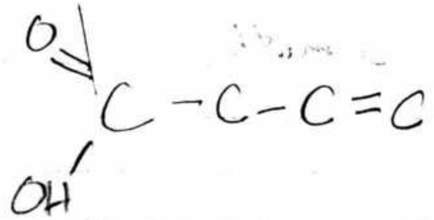
Also IR spec gives alkene @ 3080   Not bad

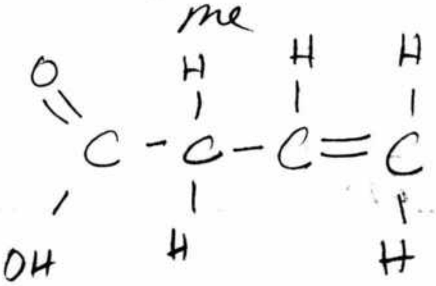
Next we have a slope break from 3000 – 2250
Carboxylic acid, IR Spec is 2500 – 3100.
Toolbox COOH is 2500 – 3300. Also on track.

Therefore we have
COOH, amine, amide, alkene ~~& COOH again~~.

[redacted]

3 ~~to~~ Butenoic Acid





Chem Spider Version

Chem formula is CH_2CHCH_2COOH

This is a corrosive organic acid.
Bad news.
Used in the preparation of pharmaceuticals
& resins

Also called vinyl acetic acid

"Terminal vinyl groups are particularly good ligands for transition metals"

Vinyl groups are commercially important since many polymers are made from vinyl monomers.

Terminal alkene is a proper phrase

Vinyl group can polymerize w/ the aid of a radical initiator or a catalyst.

Chem Spider.
Structure file
MOL, SDF, CDX

Chemspider.com
is useful & powerful

www.acdlabs.com

ACD/Chemsketch Freeware version

Chemspider is very useful

Octatrienoic acid
This has CH_3 on the end so it is not the same

but
7 Octen 4 ynoic acid
does end w/ alkene but has ≡ bond
not quite

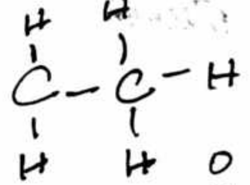
~~4,6,7 Octatrienoic acid looks close~~

~~that includes~~ acid, conjugation, & vinyl terminal alkene

ethyl 3 5 7 octatrienoate

another name is 3 5 7 octatrienoic acid ethyl ester
this provides some hits

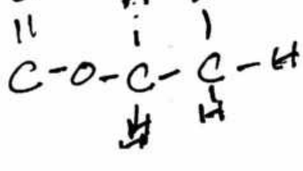
Ethyl esters in relationship to oils is a hot topic.
Ethyl is $CH_2\ CH_3$



$$\begin{array}{cc} H & H \\ | & | \\ C - & C - H \\ | & | \\ H & H \end{array}$$

Ester is


$$\overset{O}{\overset{\|}{C}} - O - C$$

ethyl ester should be


$$\begin{array}{ccccc} O & & H & H & \\ \| & & | & | & \\ C - & O - & C - & C - & H \\ & & | & | & \\ & & H & H & \end{array}$$

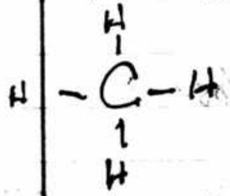
The issue here is between
TG oils (Triglyceride oils)
and
EE oils (Ethyl Esters)

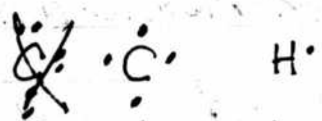
CDB "Oil" may

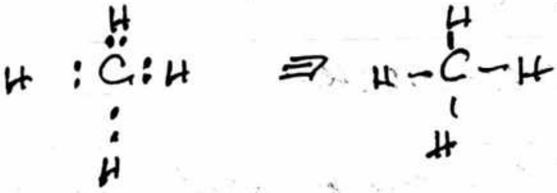
1. oxidize easily
2. Combine w/ halogens
3. metabolize poorly
4. polymerize (vinyl group)

Remember formal Charge:

$$\text{Formal Charge} = \text{Valence Electrons} - \overset{\text{(Free Electrons)}}{\text{Dots}} - \overset{\text{(Bonds)}}{\text{Sticks}}$$







$$FC = \underset{\text{Valence Electrons}}{4} - \overset{0}{\cancel{4}} - \underset{\text{Bonds}}{\overset{4}{\cancel{0}}} = 0$$ OK.

So

FC = Valence Electrons - Dots - Sticks

So

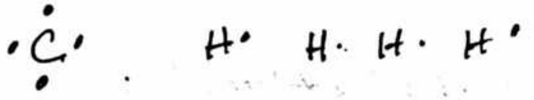
\- Sticks = FC - Valence Electrons + Dots   and let FC = 0

Sticks = Valence Electrons - Dots

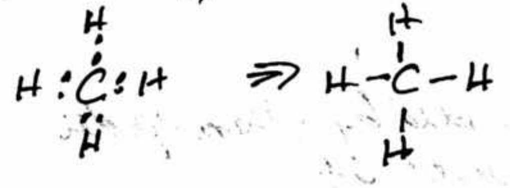
This means the no. of bonds in a neutral item is

$\text{Bonds}_{(FC=0)}$ = Valence Electrons - Free Electrons.
(~~[illegible]~~) of the central atom!!!   (Total No)

So example CH_4



~~Bonds~~= First, the molecule ~~m~~ is to be formed



4 = 4 - 0. OK   So you can always determine the no of bonds in a neutral atom.

We learned that the Valence electron in the formula FC = Valence Electrons (Central) - Bonds - Total Free Electrons.

Now notice how limited the act SPONCH is but also how important it is.

So

FC = Valence Electrons − Dots − Sticks

so

− Sticks = FC − Valence Electrons + Dots and let FC = 0

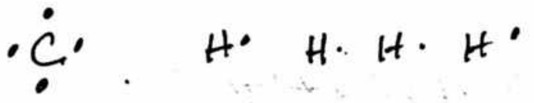
Sticks = Valence Electrons − Dots

This means the no. of bonds in a neutral item is

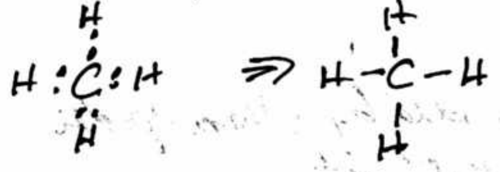
$\text{Bonds}_{(FC=0)}$ = Valence Electrons − Free Electrons. (Total No)

of the central atom!!!

So example CH_4



Bonds: First, the molecule ~~m~~ is to be formed



4 = 4 − 0. OK So you can always determine the no of bonds in a neutral atom.

We learned that the Valence electron in the formula FC = Valence Electrons (Central) − Bonds − Total Free Electrons.

Now notice how limited the set SPONCH is but also how important it is.

Page 18 Why

[redacted]

Military Communication —

how
tests
local

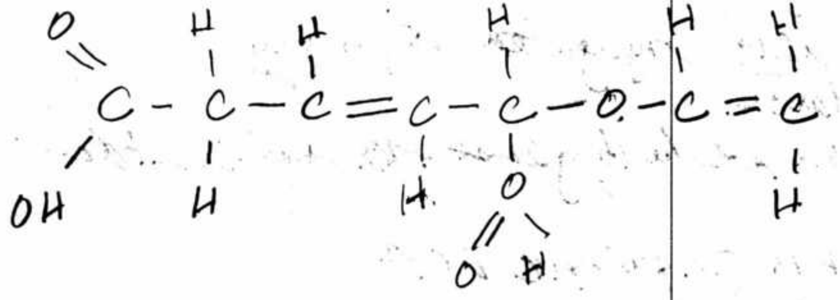
We now have the general structure in Avogadro & Chemsketch.
No hits yet.

Properties can be generated by ChemSpider
File is CDB-Proposed 04.
# of Hydrogen bond acceptors
Boiling Point 383°C
Flash Point 144°C
Index of refraction 1.5

Since nothing fits I will remove an aldehyde to see if it make it simple.

So even this failed.
Let's keep working towards a minimum.

Minimum structure:



Predicted Index of Refraction is 1.484

measured Index of Refraction is 1.488
This is quite phenomenal .

Flash pt prediction is 135.4°C
# of Hydrogen bond acceptors = 4

An acrylic acid is the simplest unsaturated carboxylic acid consisting of a vinyl group connected directly to a carboxylic acid terminus.

Molecular formula is $C_8H_{10}O_4$
Estimated Dipole Moment 0.633

The character of an acrylic acid is that of a "plastic acid", ie it acts as a vinyl (plastic) compound and as an acid.

Acrylic acid is reactive and flammable
Two main uses are in plastics & textiles

Page 20

The search for

acrylic <u>acid</u> conjugation is a very hot search.

Hemoglobin stability against thermal breakdown

actually it is polyacrylic acid.

"POLYACRYLIC ACID" is a target

What about polyacrylic acid ester & aldehyde

"Acrylic acid & its esters readily combine w/ themselves to form polyacrylic acid!
eg vinyl

It also can be used to permit biological activity of hemoglobin w/in solvents.

CONJUGATED
POLYACRYLIC
ACID.

Applications of Polymerization

*

Conjugated polyacrylic acid hot <u>button</u>

(drug delivery is an application)
"Synthesis & Characterization of Acrylic Based Copolymeric Hydrogel Nanoparticles: An Approach to Drug Delivery."

Application:
1. Stabilize blood at high temperatures
2. Allow for biological activity of hemoglobin within solvents
3. Drug delivery
4. Tissue engineering (ie, artificial tissue)

There are polyacrylic lipid conjugates

"Polyacrylic acid is a well known polyelectrolyte that responds to changes in pH by altering its physical conformation."

1. Environmental Filaments & Add. & Env. Samples
2. Biological Molecules
3. Variations in ~~Biological~~ Samples Organic (Biological)

Page
22

Fri Apr 25

[redacted]

~~th~~

I am ~~interested~~ in the formal charge [illegible].
It is crucial to the development of a molecular ~~structures~~.

Example NH_4 set to construction as smoothly as possible

What is N? N has a valence of? 5

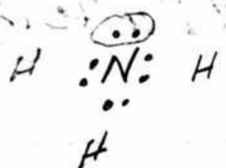
	4	5	6
H	C	N	O
		P	S

you need to know SPONCH
6 5 6 5 4 1
2 3 2 3 4 1 Bonds?

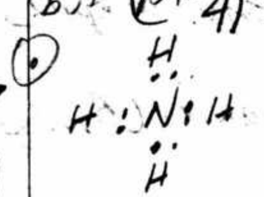
Sponch
Crops

FC = Valence − Bonds (Pairs) − Free electrons
(formal charge)

F.C. = 5 − 3 − 2 = 0



but $(NH_4)^+$ has a charge. Look @ why:



but there is an extra electron

This is apparently not retained

So what exactly happens here? ~~it appears that the extra electron~~ gets "~~stripped off~~" and reacts w/ something ~~else~~.

Look @ FC here
FC = 5 − 4 ~~[illegible]~~ = ~~0~~ +1

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Lets look @ H_2SO_4

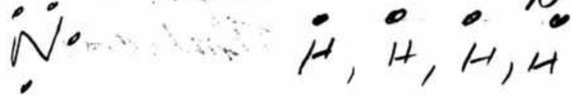
4 5 6
C N O
P S

S: Valence = 6
O: Valence = 6
Everyone wants 8
except H which wants 2

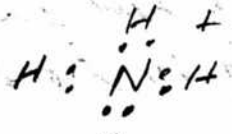
FC = 4 - 4 - 0 = 0
Valence Bonds Free Electrons

Now, back to $(NH_4)^+$ & NH_3

The charge refers to the central atom and the bonds made. Assume, for now that it is NH_4



N valence is 5



H + e⁻ →

FC = 5 - 4 - 0 = +1 This is why it has
valence bonds free electrons

a ~~[illegible]~~ polyatomic charge of +1.

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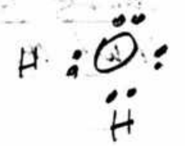
So I think that this business of formal charge is actually very ~~interesting~~?

H_2O

You know that O makes <u>2</u> bonds
Why. Because
FC = Valence − Bonds − Free Electrons
So Bonds = Valence − Free Electrons
when FC = 0
Valence of O = 6
Free Electrons = 4
So # Bonds = 2



Now go back to the geometry.
This is in Winters Org Chem book p 14.
The hybridization includes the sum of bonds <u>and</u> lone pairs
so we have 2+2 = <u>4</u>

# of Bonds + Lone Pairs	Geometry	
2	Linear	180°
3	Trigonal Planar	120°
4	Tetrahedral.	109.5°

So obviously w/ water, even though we only have 2 bonds we'll have a tetrahedral geometry of the bonds leading to an angle of 109.5°

The Org Chem workbook is excellent. It gives you what you need to know.

Also an interesting section on the dipole moment, even if qualitative. It is a predicted property of your molecule. How to interpret the [illegible] now?

This is amazing & you have my started. *

So many things can be learned from molecular structure.

There is so much that can be learned when you have a molecular structure.

Page 25

1. You can assess electronegativity.
2. This leads to bond types: covalent, polar covalent or ionic (% ionic also)
3. This leads to conductivity expected.
4. Then you have dipole moments
5. And Lewis structures
6. And formal charge determination
7. And geometry of the molecule
8. And hybridization.

This is also very cool, P 76 EZ Chemistry is the best

9. And solubility, and melting & boiling points likely.
10. And index of refraction along w/ a whole host of predicted properties including dipole moment. See Avogadro & ChemSketch software
11. And Lewis structures gives lone pairs & lone electrons for that matter.

Sources:

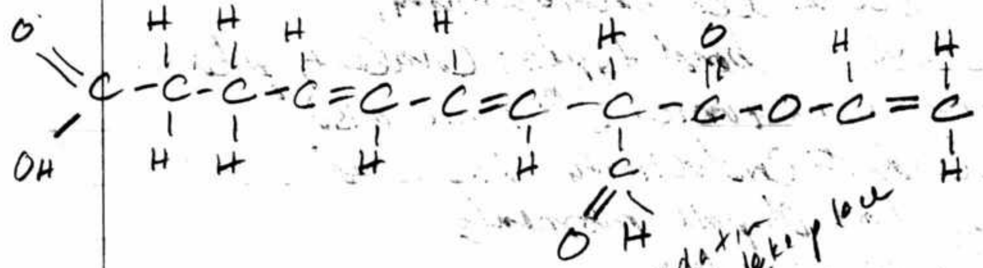
1. Org Chem Workbook (Winter)
2. Barrons EZ Chemistry
3. All the Laminated Charts
4. Chemical Suite Software
   Postscript

12. And we have now moved into acid-base chemistry which is very cool and fundamental to organic chemistry reactions.

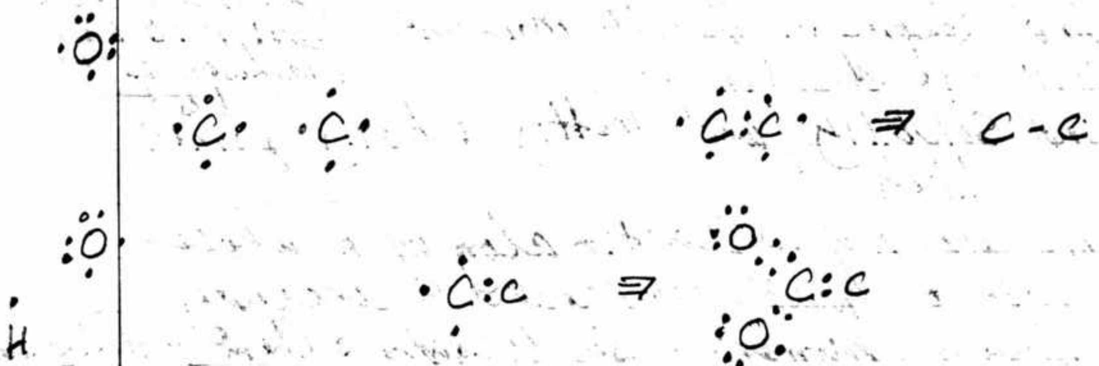
Structural Prototype

Page 26

So we have a proposed initial structure for CDB Lipids. Let us look @ these methods in relation to the structure.



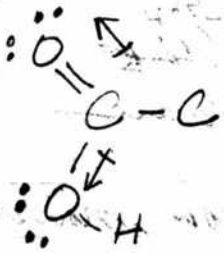
What about COOH?



Now to:

and this is it.

and this leads to:



Now lets look @ formal charge and dipole moments, geometry.

FC of the double bonded oxygen:

(formal charge) FC = Valence − Bonds − FE (free electrons)

6 − 2 − 4 = 0.

Dipole Moments. Double bonds are stronger than single bonds, etc.

C electronegativity is 2.5

O is 3.5

Δ = 1.0 polar covalent toward the oxygen. and the fact that it is a double bond should make it even more so.

So the double bonded Oxygen should have even a stronger dipole moment than to the single O and this should leave the carbon of the COOH group w/a net dipole moment in the direction of the double bonded oxygen. Both oxygens have 2 sets of lone pairs which I believe should also make them more reactive.

A C-O bond is 21% ionic in character

(ie 79% covalent in character).

What do lone pairs really signify?

Is it essentially reactivity?

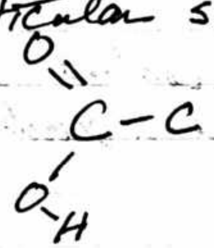
Remember your statements that chemistry is primarily about the reactions that take place with electrons?

The bond dissociation for a double bond, except for O=O & even a triple bond looks to be roughly a linear relationship

Page 28

A really interesting question, therefore, is what type of reaction does an acid group become involved with?

But before we do this, what is the total bond ~~[illegible]~~ dissociation (notice the spelling!) energy of this particular sub molecule?



	kJ	n
C-C	347	1
C-O	358	1
C=O	745	1
O-H	467	1
	Σ 1917 kJ	

EZ p76 has the best geometry page

p14 organic chem workbook simplifies

What is the geometry of this bond?

!!!

To know this, we need to know the ~~sum~~ number of atoms bonded & the no of free PAIRS of electrons.

Here we have 3 attached atoms & no free pair of electrons.

So this should be trigonal planar geometry.

I would think that the double O=C bond affects ~~the~~ geometry to some degree.

Look @ prob 11, p15 Org. Chem Workbook (WB)

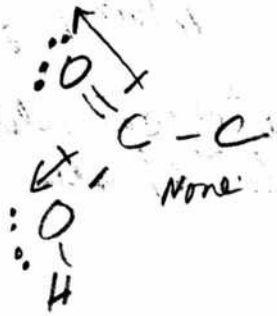
But notice ~~that~~ he did not make any distinction or allowance for the C-C=C double bond. He did not say it changed anything. Keep your ear tuned on this one.

* A remaining question is what is the importance & significance of lone pair of electrons in the molecules.

* The next question is what do acids do!

* and what about solubility of this molecular group? p12 Org Chem WB brings up this subject. What is a dipole moment?

Also whatever happens we see that it has a dipole moment in the direction of the Oxygen. I would think the dipole moment would look something like



for a sum effect of

and we have lone pairs.

Page 30

We already know that lone pairs affect the geometry of a molecule & that they serve to deflect (or bend) the [illegible] bonds of a molecule as if they were actual bonds.

They are also going to affect resonance of ~~structure~~s.

In next two pages We see how that they are intimately connected →

So we want to know about lone pairs and acids now.

"Valence electrons that are not used for bonding are called lone-pair electrons."

Note

"They are often crucial in chemical reactions"

Yes, just I supposed, so this is a key important topic to come.
Murray

"We'll soon see that the acid-base behavior of organic molecules helps explain much of their chemistry" Murray p18

Essentially all biological reactions involve organic acids & bases.

There are powerful statements taking place now.

Organic acids are characterized by the presence of a positively polarized hydrogen atom.

Carboxylic acids are involved in almost all metabolic pathways.

* So organic! acids have a positively polarized hydrogen atom.
* Organic bases have a lone pair of electrons that can bond to H^+.

Some oxygen containing compounds can act as both acids & bases.

A Lewis acid is a substance that ~~donates~~ accepts an electron pair.

A Lewis base is a substance that donates an electron pair

[The donated pair is shared between the acid & base in a covalent bond. This means that they go together <u>as a</u> set.]

This is already getting interesting. Many metal cations (think Fe^{+2}) are Lewis acids because they have unfilled valence orbitals and they can accept electron pairs from Lewis bases (how about oxygen?)

Page 32

Now you are seeing why H_2O can act both as an acid & a base.
It has the polarized positively hydrogen atom.
It has oxygen w/ free pair of electrons.

* "In general, most oxygen & nitrogen containing organic compounds act as Lewis bases because they have lone pairs of electrons."

So now you can see the importance of lone pairs. They act w/ as a base & they react with an acid (such as a metal cation).

An example of a Lewis Acid & a Lewis Base Pair

HCl H_2O

EN of Cl is: 3.16
H is 2.20
$\Delta E \cong 1.0$
So water is polar covalent

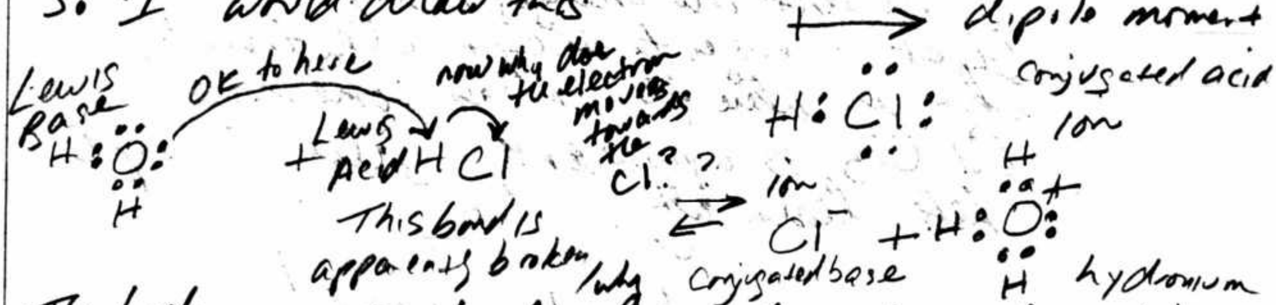
Oxygen has lone pairs here. So it can act as a base

Water is 76% Covalent

Page 33

So HCl is a perfect candidate to act as a Lewis acid and a base.

~~the water is the acid.~~ The HCl is the acid
The oxygen in the water acts as a base.
So I would draw this



The hydrogen is positively polarized so it wants to accept ~~the~~ an electron.

Murray does not show the details of this

In Barrons the Ez way p16 he uses the phrase "the _ ion followed along to balance the charge"

Maybe this is what is happening?

What Barrons Ez way says is that the HCl bond is broken. I do not know why.
Notice it always acts as an internal set.

Lets toy with the idea of Fe^{+2} & COOH ...

Ok, now we understand Lewis acid better. Although it is often containing a polarized (positively) hydrogen atom it does not have to be this. It can also be an atom with a

"vacant low energy orbital"
(that is eager to accept electrons".
This is where the metals come in.
AlCl3 is apparently a great example.
Lets learn why.

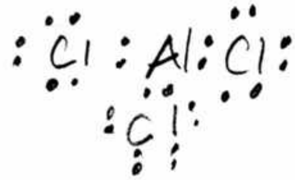
Al is a transition metal!
What is the electronic configuration of Al?
Transition metals can have up to 18 electrons in the outer shell.

Al: $[Ne]3s^2 3p^1$ Has 3 electrons in the outer shell

Fe: $[Ar]3d^6 4s^2$ Has 2 electrons in the outer shell

So even w/ the octet rule, Aluminum is after a lot of electrons. It only has a valence of 3

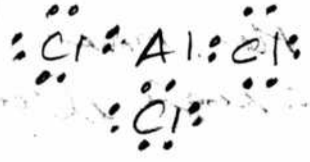
$AlCl_3$



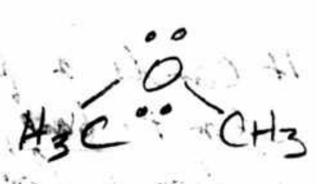
You see that Al still wants electrons. So $AlCl_3$ is very acidic.

Page 35

If we have



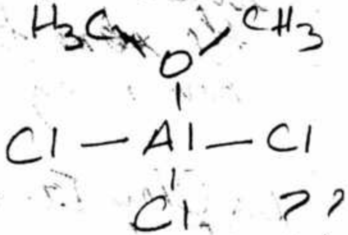
and we have



We should know that an electron from O wants to move over to the aluminum. But don't both O electrons want to move over?

Unknown if this is correct. ??

???



???

No answer in the book.

Regardless if you are right or not on this formation, you are seeing that many of the metals are very hungry for electron. & this makes them acidic.

Davis - Great Courses is going to introduce reaction mechanisms to us.

Relocation of electrons causes bond change, a reaction "make & break bonds"

He is working through the formation of urea.

$NH_4NCO \rightarrow (NH_2)_2CO$ Generic scheme

Next is Haber Prosch Process' is next example.

Page 36

Davis is now showing an mechanism example

It can be a pair of electrons that move from the base, not just the a single electron from a lone pair.

It somehow is forming a new bond & breaking an existing bond @ the essentially the same time, I am not sure exactly how or why this is happening.

Org Chem EZ tries to show me in detail how this happens also on p 65

Today we study reaction mechanisms Also Acids & Base & Workbook.

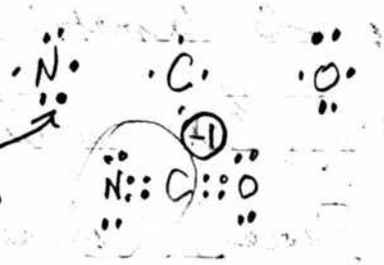
Davis gives us the reaction in more detail now

Notice NH_4 will have a positive charge to it.

FC = 5 - 4 - 0 = +1

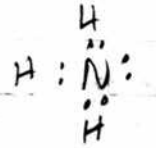
$\ddot{N}=C=\ddot{O}$

Lets expand this



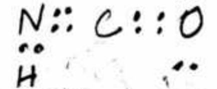
an extra electron is here

Postscript:
So this all leads to:



FC = 5 - 3 - 2 = 0

and



$FC_N = 5 - 3 - 2 = 0$

Notice this, very interesting here.
The only way that N can have a double bond with C and still have 4 electrons available as Davis provides in Lec 4 @ $27^{m}13^{s}$ is if the N=C=O group has an extra electron on the N. This will give it a negative charge which ~~that~~ is why it is prone to react with the NH_4 that has a positive charge.
Check ~~it~~ this:
FC of $\overset{\cdot}{\underset{\cdot\cdot}{N}}=C$

FC = 5-2-4 = -1 <u>yes</u>
So this is why an electron wants to move from

$\overset{(-1)}{\underset{\cdot\cdot}{\ddot{N}}}=C=O$ to the $NH_4^{(+1)}$ This is great!

Also remember the NH_4 has no dipole moment here but it does have a charge of +1.
N=C also does not have a strong dipole moment but it has a charge of -1.
So, the electron wants to move!

This leads to some kind of switcharoo effect that I also do not understand yet.

Well, we know that the $NH_4^{(+1)}$ wants to become NH_3 neutral! We know that the $N{=}C^{\ominus}$ wants to become neutral. So how does this happen.
The NH_4 gives up a hydrogen (not the electrons, just the hydrogen. The N=C accepts the hydrogen (proton) not the electrons.

So it is the proton (hydrogen) only that moves & adjusts!

This is very cool. This starts to demonstrate how electrons (or protons, for that matter) move to cause a reaction.

Davis is now talking about acids.

a powerful Statement

"The transfer of protons ~~to~~ from acids to bases (is by far the most common and arguably the most ~~important~~. influential reaction in all of organic chemistry)."

Bronsted Lowry ~~metho~~ model:
Acids donate protons (H+)
Bases accept protons

The loss of a proton by an acid always produces a conjugate base.

A more ~~stable~~ stable conjugate base means a stronger acid.

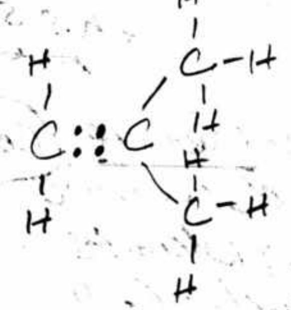
So what does a "stable conjugate base" mean?

Factors are 1. Electronegativity
2. Nearby pi systems providing the stability of resonance

P69 Org Chem E2

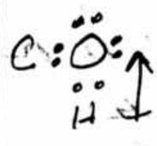
Polymerization of alkenes with Acid

Now we are getting involved w/ polymerization.

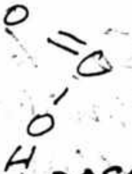


An alkene:

The double C bond is rich in electrons. It acts as a base.



EN of OH: $O = 3.5$
$H = 2.1$
$\Delta = 1.4$

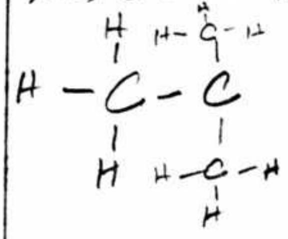


positively

C-OH

We see that OH is a polarized hydrogen. This makes it an acid.

This should lead to:



But now the C on the right has a FC of

FC = 4-3-0 = +1

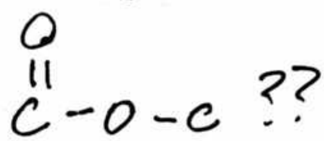
So now it has a charge of +!.

So it wants an electron.

Where will it take it from? Another molecule!

I now understand how a polymer can form from an alkene in combination w/ an acid i.e., the OH group.

It could also get other electrons from the ester group



$\overset{O}{\overset{\|}{C}}-O-C$??

[redacted]

Maybe also from the aldehyde?

From Free Radical pdf:

this should mean O_2

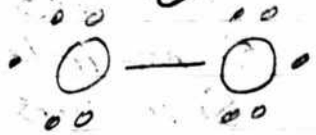
"Oxygen is a relatively unreactive compound that can be metabolized in vivo to form highly reactive oxidants known as oxygen free radicals".

he is talking about O_2 here I believe not O

So, to begin with, is oxygen reactive or unreactive? Sure seems like it is reactive to me ... rust, etc? ..

But oxygen is highly electronegative. Seems to me this makes it ~~unreactive~~ reactive.

The actual structure of O_2 is



and this structure is unusual!
It does not have a double bond.
This structure would indeed be relatively unreactive but O as an element is not unreactive, IT IS REACTIVE.

Now remember that free radicals have

Developing Topics : Apr 30 2015
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N. California

1. General molecular assessment is very interesting and powerful as a foundation of understanding a structure.
This is on the star page about 8 back. *

2. We now understand how polymerization take place between acids & alkenes.
This has major implications.
It will need to be proven w/ better instrumentation.

3. We need now to look at additional functional groups including aldehyde & esters.
What might they mean or bring?

4. We need to continue analyzing spectra
- You are starting to get good @ it and you have good offline tools now. (derivative analysis)
2 offline software programs & Koji

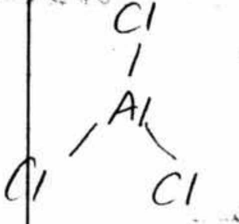
5. What marvelous ACD molecular editing capability you have now along w/ search capability: Avogadro & ACD.

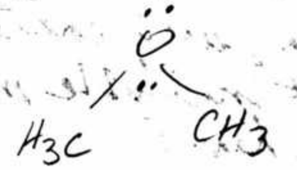
6. You have the free radical paper that you really need to understand. Remember the lipid peroxidation issue in conjunction w/ free radicals?

Page 42

7. You should also be able to look @ how metals might attack now. via acid - base chemistry
8. Acid base chemistry is fundamental toward understanding of organic chemical reactions.
9. We can see that the Org Chem WB is really useful. Working on problems forces you to truly understand how to use the material vs just read it.

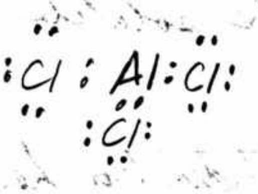
Org Chem WB. Lets look @ Prob 3 p 63 again
I am sure you do not have a full understanding here.





Now lets look @ these w/ greater attention.
Al has a valence of 3. Chlorine has a valence of 7

so what would $AlCl_3$ look like



Notice the Al does not have a full octet here
So it seems to me it would like to
have more electrons what about dipole
moment, formal charge, geometry?
% ionic, solubility, etc?

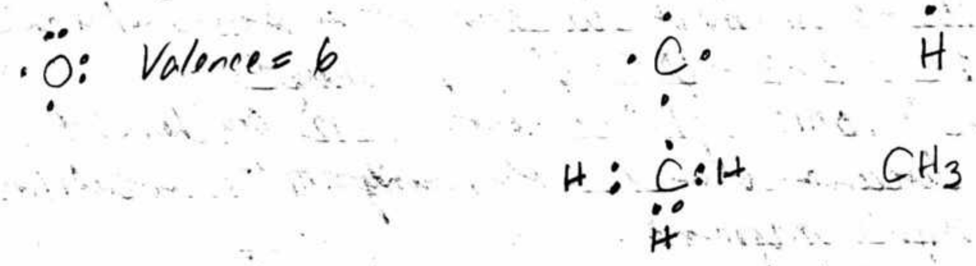
ΔEN = 1.61
— 3.16 = >1 <2 polar covalent.
Let's really start studying the properties of a molecule
it really helps toward understanding.
What is the geometry?
No of bonds + electron pairs (free) = 3 so it
should be trigonal planar. Therefore there is no
dipole moment because it is symmetrical.
FC = 3 - 3 - 0 = 0. No charge
28% Ionic, 72% Covalent. p12 Org Chem WB
discusses this from the standpoint of solubility &
dipole moment.

"It's hard to get a reaction between two
molecules that don't dissolve in the same
solvent."

So let's start thinking about this.
What happens w/ C-H bond?
ΔEN = 2.55 - 2.20 = .35 (ie a non polar covalent bond)
This is almost a purely covalent bond.
So there is almost no dipole moment.
Water on the other hand:
EN Δ O-H = 3.44 - 2.20 = 1.24 this is polar covalent.
So this is why oil & water do not mix.
Now back ~~to~~ ACl_3
No dipole moment. ΔEN = 1.55
This is definitely polar covalent. This would indicate to me that ACl_3 should be soluble in water to an extent. Test it.

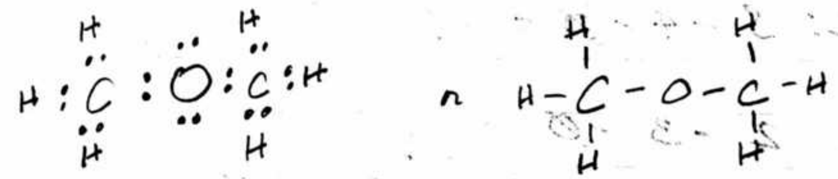
Yes, it is soluble. This was very good deduction here. Both water & $AlCl_3$ are polar covalent even though there is no dipole moment in $AlCl_3$.
So now we know quite a bit about $AlCl_3$ but we notice that it does not have a full octet.
Let's see where this leads.

Now to $O(CH_3)_2$

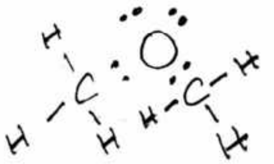


P63 Org Chem WB. I think I have it right!

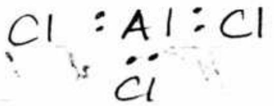
Now when we combine $O(CH_3)_2$



and it actually creates a bent structure.

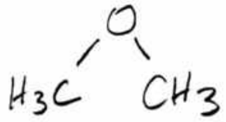


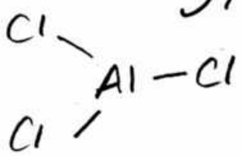
So we have two lone pairs acts as a base



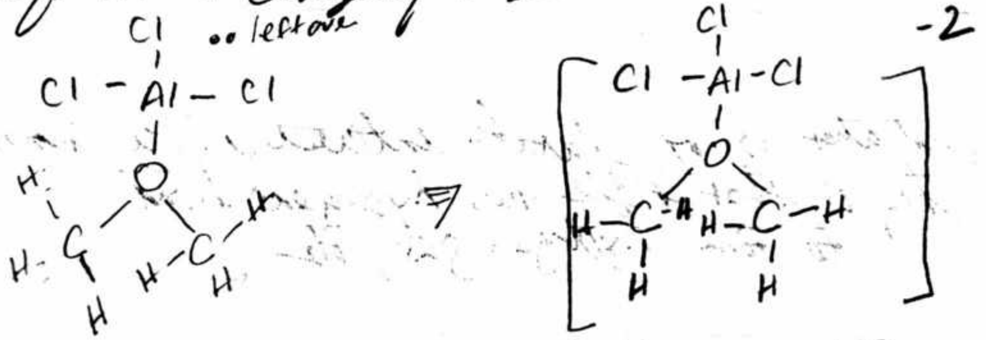
Trigonal planar

Now, bases donate electrons $O(CH_3)_2$
Acids accept electrons $AlCl_3$
Geometry of $O(CH_3)_2$
No of σ bonds = 2 no of electron pairs = 4
should be tetrahedral in theory, and bent in practice





Now it seems to me that the $AlCl_3$ would like to join to get an octet. Seems to me it would be left with a charge of -2



Is this correct?

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Lets compute the FC properly:

Al FC: 3 − 4 − 0 = −1

O FC 2 − 3 − 0 = −1

$\Sigma = -2$ great.

Let's move on to Prob #4

H^+ & $:H^-$

Start with

H^+ this is a proton, so it is missing an electron
this is an acid

$:H^-$ has an extra electron
Since it has a pair of electrons to donate
it acts as a base.
So it forms

H• with no charge

$:H \quad H \rightarrow H\cdot + H\cdot$

and what is of further interest in the answer key is that the two hydrogens bond to form hydrogen gas, H_2

H — H

So this is good, you are starting to see the power and advantages of acid-base chemistry. Any time (and that is a lot of times) that there are electron pairs floating around or if you have a positively charged hydrogen in the mix, you will have acid-base chemistry.

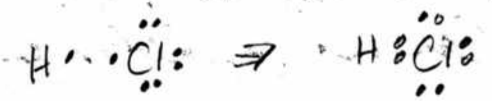
Now we get to compare acids. Davis does this also.

"The loss of a proton by an acid always produces a conjugate base."

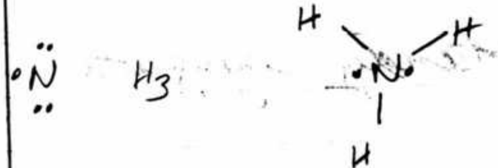
Next: The more stable the conjugate base of an acid, the stronger the acid.

First, what is a conjugate base? The deprotonated form of the acid.
EZ Chemistry (red) p 242
Lets look @ the case of HCl & NH_3

$FC = 7 - 1 - 6 = 0$ OK —



H only wants 2 electrons, all OK



Formal Charge $= 5 - 3 - 2 = 0$ OK

So nitrogen acts as a base, ie it donates electrons
ΔEN HCl $= 3.16 - 2.2 \cong 1.0$ so this is polar covalent
The H in HCl is partially positively polarized, this means it acts as an acid.

Sec 1.1.1 Murray p 22 lays out the foundation for acid-base chemistry — Organic Acids & Organic Bases

Back to Murray p22
Organic
Acid: presence of a positively polarized hydrogen atom
(usually O-H and
O=C-C-H)
COOH is very dominant.

What Murray says is that bases have a lone pair(s) of electrons that can bond to H^+.

Interesting that a lone pair is required to when it seems like a unpaired electron would also do the trick. Never the less the emphasis seems to be upon available lone pairs. O & N fit the bill perfectly. Nitrogen containing ~~so~~ compounds are the most common to act as base but O also can (2 pairs) N has one pair. (Interestingly enough O can act sometimes as an acid as well.)

Now back to understanding conjugate acid and base.

In an acid base reaction, the acid gives up a proton and becomes the conjugate base.

The conjugated base, BY DEFINITION, is the deprotonated acid.

Summary: The deprotonated acid <u>IS</u> the conjugated base

Conjugate Acids & Bases

Let's now revert to the $HCl + NH_3$ reaction. We know that the HCl is the acid from a couple of pages ago and we know that NH_3 is a base because it has a lone pair of electrons available.

Now, the reaction is, and I am not sure how I would know that, is:

$$HCl + NH_3 = Cl^- + NH_4^+$$

So in this case, Cl^- IS the conjugate base and NH_4^+ IS the conjugate acid.

Think about it, Cl^- now has an extra electron available, so it can now act as a base. (And this statement confirms that it DOES NOT have to be a lone pair, it can be a lone electron as you were wondering earlier)

And in return the NH_4^+ has a partially positively polarized hydrogen atom (recall EN: $3.04 - 2.20 = 0.8$ means just barely polar covalent) so it can now act as acid, and it is the conjugate acid.

So this is a real switcharoo effect

Very interesting.

Now let's understand the HA terminology.

Page 50

Back to the HCl NH$_3$ issue.
It looks like what happens with HCl is

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

and then it seems that

$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$

and that water is transparent to the reaction
and we are left with
$HCl + NH_3 \rightarrow \underline{NH_4^+} + Cl^-$

"A given acid, HA"

so an acid can be called HA
Why? because what matters is the available
partially polarized hydrogen atom that
allows ~~an electron to be taken away~~ proton to be donated.
So HA is legitimate terminology

In water:
$HA + H_2O \rightarrow A^- + H_3O^+$

exactly what you just looked @ w/ HCl.

We certainly now also understand

$$K_A = \frac{[A^-][H_3O^+]}{HA}$$

(remember that apparently we leave out the water).

So now we understand conjugate acids & bases better (it's the old [illegible] effect)

as well as HA terminology
This is all very good.

Now we can move on again to Org Chem WB page 63 on "Comparing acidities of Organic Molecules"

4 Rationales as to why one acid is stronger than another:

Note: Atom size trumps electronegativity in the process we are about to learn.

I think an example will be better to learn w/ for now.

Ok, lets go. HCl or HF

Which is stronger and why?

~~Pro~~

Proton Transfer Reaction

Davis says that it is the "exchange acid & a base exchange one simple hydrogen nucleus (ie, proton).

Page 52

Acid base Chemistry, by known observations, depends upon POSITIVELY CHARGED. HYDROGEN IONS.

For the sake of convenience and simplicity we will call them PROTONS because they are structurally equivalent to that form

Bases LOWER THE CONCENTRATION of hydrogen ions

(water pronunciation)

Acids(HA) will dissociate into a proton (H^+) and a Conjugate base (A^-)

Smaller pKa means a stronger acid.

Ka of the dissociating acid

$$K_{eq} = \frac{Ka(HA')}{Ka(HA')}$$

equilibrium

he has different colors

newly formed Conjugated acid

Then will likely become important

Deltermines how equilibrium shifts in the reaction.

We can use a product form

$K_{eq} = K_{eq} * K_{eq}$

equilibrium

citric acid + fish smell

$K_{eq} = 10^{-3.2} \cdot 10^{10.6} = 10^{7.4}$ reaction is highly favored to the right

Citric Acid + Methyl Amine ⟷ dihydrogen Citrate + methylammonium

pK 3.2 pK = 10.6

Predicting Acidity in Comparisons

1. Assess the stability of the Conjugate base.
Two factors:

one set
1. Electronegativity
~~2. Nearby pi systems.~~
2. Quantity
3. Proximity

Resonance

This is a more complex topic

Monoprotic vs Polyprotic acids

depends upon how many acidic hydrogens are attached, it is not always one.

So polyprotic can have very important ramifications.

More than one disassociation is involved.

Now we return to Org Chem WB and the comparison of acids.

Back to the example problem p 64
Which acid is stronger, HCl or HF

$\mathrm{H{:}\overset{..}{\underset{..}{Cl}}{:}}$ $\qquad$ $\mathrm{H{:}\overset{..}{\underset{..}{F}}{:}}$

ΔEN HCl: 3.16 - 2.20 = 0.96
ΔEN HF 3.98 - 2.20 = 1.78

HF is definitely more electronegative

But guess what, this is not the problem.

The question is HF or HI, so

ΔEN: HI = 2.66 - 2.20 = 0.46

and HI $\quad$ $\mathrm{H{:}\overset{..}{\underset{..}{I}}{:}}$

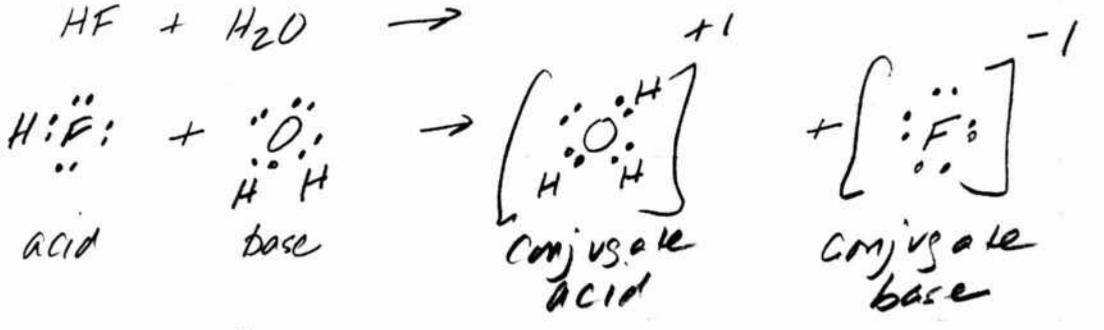
[redacted]

Acid Comparisons
A Useful Skill

Page 55

So the first thing we must do is to "deprotonate" the acid. The only way that makes sense to do this is in water.

$HF + H_2O \rightarrow$



FC FC FC FC

$7-1-6=0$ $6-2-4=0$ $6-3-2=\boxed{+1}$ $7-0-8=-1$

Now, the big news is that the strength of an acid depends upon the stability of the conjugate base. We should have the same general relationship w/ I so we should be left with:

$HI + H_2O \rightarrow H_3O^+ + I^-$

So Factors: EN of F = 3.98
EN of I = 2.66

Fl is more electronegative but remember atom size trumps electronegativity

Atomic radius of F is 0.64
" " I is 1.33

I is bigger. Atom size trumps electronegativity so HI is a stronger acid than HF

Great - my 1st acid comparison.

Page 56

Now we go back to HCl and HF.

We have the same structure taking place

$HCl + H_2O \rightarrow H_3O^+ + \overset{\text{conjugate base}}{Cl^-}$

EN of Cl^- is 3.16

$HF + H_2O \rightarrow H_3O^+ + \overset{\text{conjugate base}}{F^-}$

EN of F^- is 3.98

so F is more electronegative but

A.R of Cl^- is 0.99 angstroms

A.R of F^- is 0.64

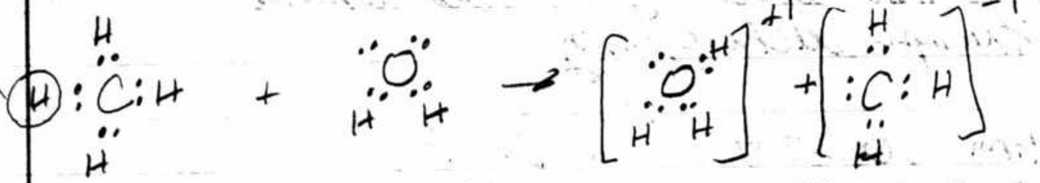
Conjugate Base Analysis:

So Chlorine is both more electronegative and larger so I say HCl is a stronger acid than HF.

Answer: HCl good job.

Next one:

CH_4 or NH_3??



only the nucleus actually moves which is H+

FC = 4 - 3 - 2 = -1

acid

base

FC = 6 - 3 - 2 = +1

conjugate acid

FC = 5 - 2 - 4 = = -1

conjugate base

Conjugate base analysis:
ΔEN of CH = 2.55 - 2.20 = 0.35

ΔEN of NH = 3.04 - 2.20 = 0.04

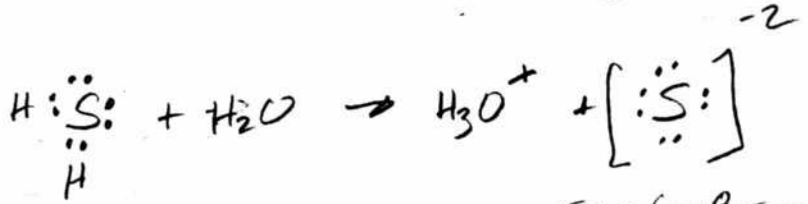
So NH is more electronegative.

I do not think atom size is a big factor here so
I think NH_3 should be the stronger acid?

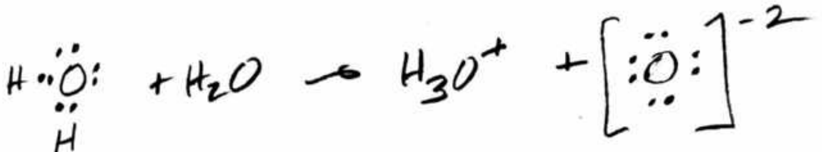
Answer: yes, my reasoning was perfectly sound & correct.

Onward to the next one:
H_2S or H_2O?

Conjugate base



FC = 6 - 8 = -2



FC = 6 - 8 = -2
Conjugate base

The oxidation state can exist.

EN of S is 2.58
EN of O is 3.44

O is more electronegative

AR of S is 1.04
AR of O is 0.66

Size trumps electronegativity.

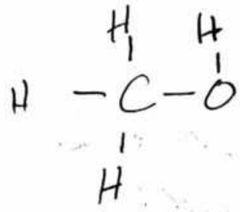
H_2S is more acidic

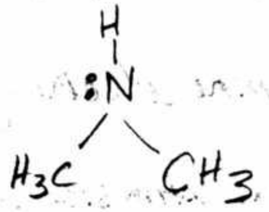
Answer H_2S OK

On & Forward:

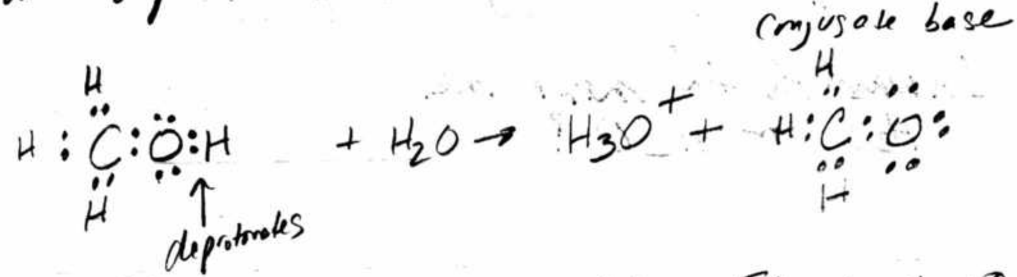
CH_3OH & $(CH_3)_2NH$

Lets go after structure first.





On CH_3OH, the OH group is polarized so this is where deprotonation occurs.



C: FC = 4 - 4 - 0 = 0
O: FC = 6 - 1 - 6 = -1

ΔEN C-O = 3.44 - 2.55 = 0.89
AR of O is 0.66 not large

Now for CH_3NH
The H on the N is polarized.

$(CH_3)_2NH + H_2O \rightarrow H_3O^+ + [(CH_3)_2N]^{-1}$
FC of N: 5-2-4 = -1

EN of N is 3.04 vs O of 3.44
AR of N is 0.70 vs O of 0.66

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This one seems like a very close call and that the two acids should be very close to one another. If size truly does trump EN in all cases then $(CH_3)_2NH$ wins but I have to wonder if the ΔEN has the greater effect here w/ the OH in CH_3OH.

Seems like a very close call
Yes, sure enough. In this case ΔEN has more influence that ΔAR as the difference is much greater w/ EN. He essentially says that the AR is the same size.

from a rough percentage point of view:

ΔEN

$$\frac{3.04-3.44}{3.24} = 12.4\%$$

(avg)

ΔAR

$$\frac{.66-.70}{.68} = 5.9\%$$

EN influence is on the order of 2 to 1 compared to AR influence.

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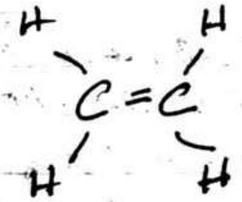
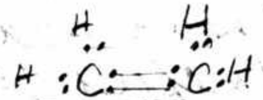
On and forward:

$H-C\equiv C-H$ vs





Before we go further,
What is the geometry of these molecules?

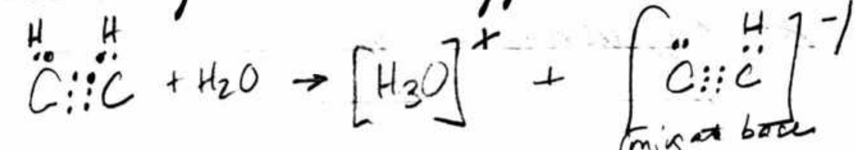
C_2H_2
No of bond @ C = 2
No of free electrons = 0

C_2H_4
No of bonds @ C = 3
No of free electron pairs = 0

Geometry is linear,
@ each C.

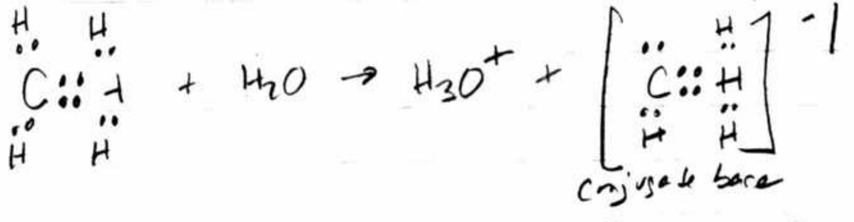
Geometry Trigonal Planar
@ each C

Is there a dipole moment. I say
ΔEN C = 0
ΔEN CH = 0.35
So there is a slight one. But it is really small.
Does it deprotonate? I suppose that it can.



FC@C = 4-4-0 = 0

FC@ left C = 4-3-2 = -1



FC@ left C =
4-3-2 = -1.

[redacted]

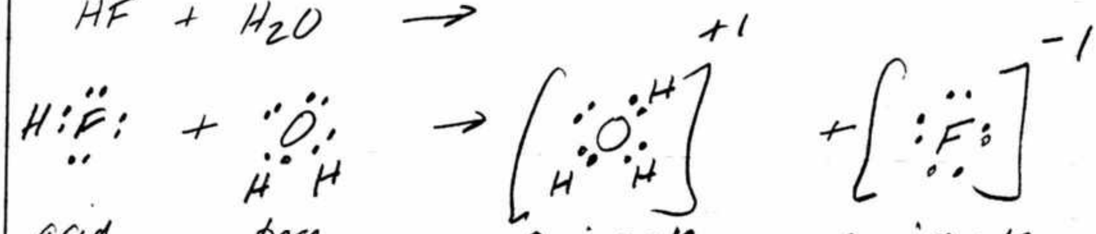
Organic Acid Comparison

A Useful Skill

Page 55

So the first thing we must do is to "deprotonate" the acid. The only way that makes sense to do this is in water.

$HF + H_2O \rightarrow$



acid　　base　　conjugate acid　　conjugate base

FC　　FC　　FC　　FC

$7-1-6=0$　　$6-2-4=0$　　$6-3-2=\boxed{+1}$　　$7-0-8=-1$

Now, the big news is that the strength of an acid depends upon the stability of the conjugate base. We should have the same general relationship w/ I so we should be left with:

$HI + H_2O \rightarrow H_3O^+ + I^-$

So Factors: EN of F = 3.98
EN of I = 2.66

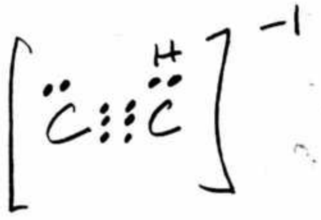
Fl is more electronegative but remember atom size trumps electronegativity

Atomic radius of F is 0.64
" " I is 1.33

I is bigger. Atom size trumps electronegativity so HI is a stronger acid than HF

Great - my 1st acid comparison.

So now we are led to the question of which is more stable:



or

~~This is a case where the no. of atoms would seem to play a role. The structure on the right would seem to be more stable since it has more atoms & therefore mass. The electronegativity & atom size does not seem to be a factor here.~~

not a factor!

No, NOT TRUE!

The left structure is more acidic. Let's learn why & then figure out ~~how~~ no. of atoms may have influenced the picture.

The answer has to do with sp^2 vs sp^3 orbitals.

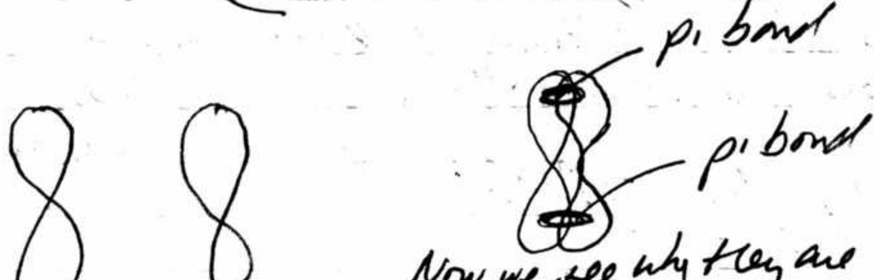
So guess what? It's time to learn what sp^2 & sp^3 really means.

Hybridization:
Davis talks about this in Lec 02.
It starts about 24 minutes in.
Atomic orbitals is the topic.

Everybody contains an S orbital
S can only hold 2 electrons.

sigma bonds

This is also a sigma bonds



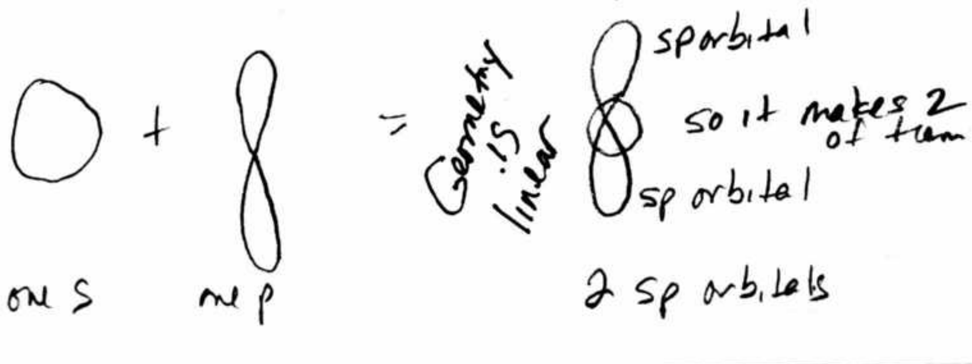
Now we see why they are two.

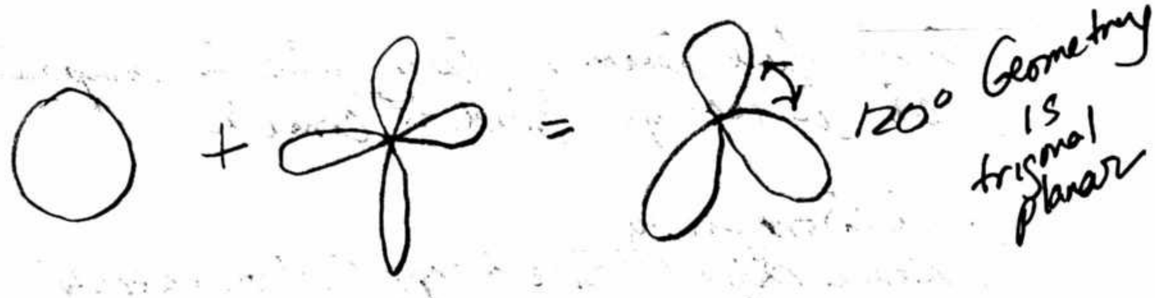
These overlap to produce pi bonds.
Do you see now why a pi bond is a double bond?

degenerate mean @ the same energy level.

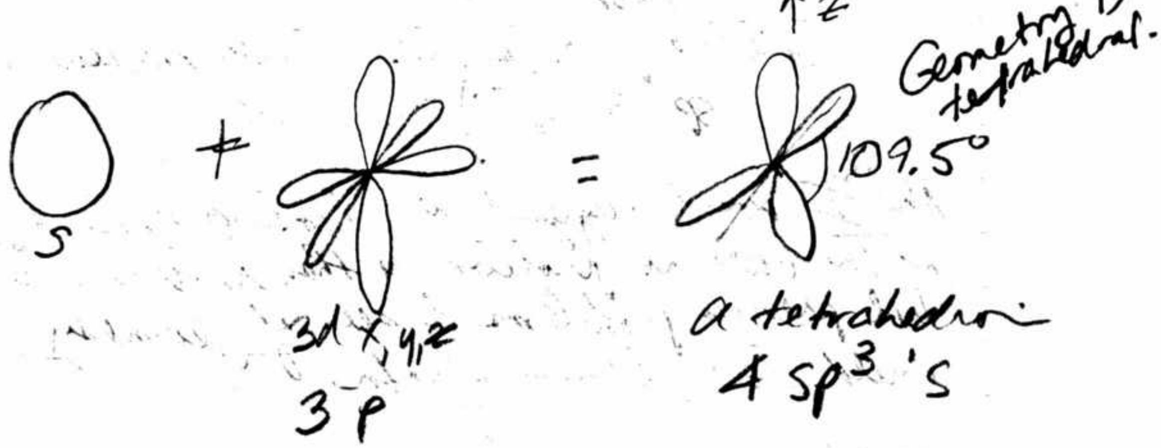
S + p = 2 sp orbitals

one s + one p makes 2 sp orbitals.
(Sort of an avg between the two)





S + 2p = 3 sp^2's



So when someone says sp hybrid, it means <u>two</u> average orbitals because they combine & linear geometry

When someone says sp^2 hybrid, it means <u>three</u> average orbitals because they combine and trigonal plana geometry

When someone says sp^3 hybrid it means 4 average orbitals have been formed because the s always combines w/ ALL of the p's. P's are dumbell, S is spherical. The geometry of these orbitals is tetrahedral.

OK, this is all better

So the first lesson of being able to compare acids so that you need to consider

1. electronegativity
2. Atomic radius (Size trumps electronegativity)
3. Geometry of the molecule. We want more S character.
Negative charges are more stable on
sp than sp^2
(the lone pair is closer to the nucleus in
sp vs sp^2)

Now I would suggest we look @ geometry of the current problem & then return to the previous problems & see if geometry could have been a factor.

So how do you determine geometry
1. No of bonds
2. Lone pairs
3. Theoretical vs visual

The best picture of geometry remains in EZ Chemistry p 76. It really is excellent & includes the effect of lone pairs.

Ok, lets look @ geometry:

sp geometry

or

sp^2 geometry

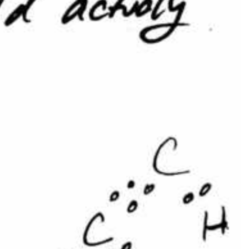
So, what is this geometry?

The left Carbon has 1 bond + 1 lone pair. This would seem to be linear to me because the electrons on the left would move as far away from the triple bond as possible. Yes, so this is sp also.

The right Carbon: has 2 bonds & no lone pairs. This would also be a linear geometry. So this would be sp geometry (two bonds).

And Org Chem WB agrees w/this. So I think it would actually look like

sp



sp^2

This is the more acidic molecule.

The left Carbon has 2 bonds & 1 lone pair. This would be trigonal planar (but also bent). This is sp^2 geometry.

The right Carbon has 3 bonds & no lone pairs so it is also trigonal planar, which is also sp^2.

And the rule is that negative charge like to be placed in orbitals w/ more s character ie.

$sp < sp^2 < sp^3$

more s character

less s character

of the conjugate base
So the factors of acidity comparison are:

1. Electronegativity
2. Atomic radius (size trumps electronegativity, at least generally on a % basis).

3. More s character in the bonds is preferred over p character

$sp < sp^2 < sp^3$

this has
more s
character
50% s
character

than this
does
25%
s
character.

And now we go on to problem 10.

S/no But Sure I Get These

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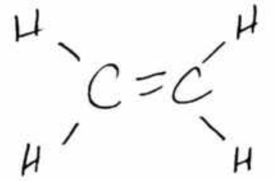
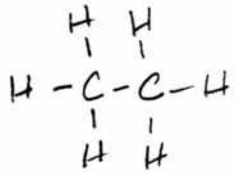
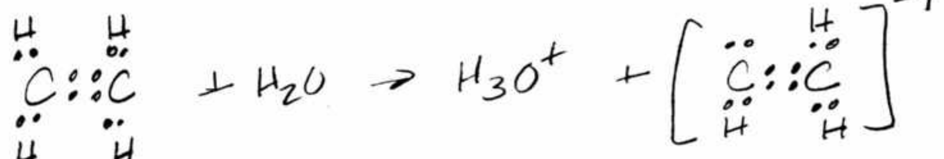
Continuing acid Comparisons - the last example for now.
Org Chem WB p 65 No 10.

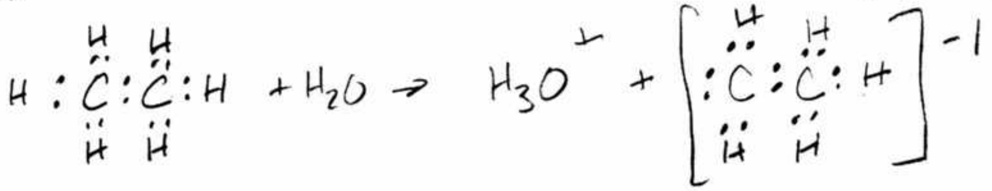






FC=4-3-2=-1
FC=4-4-0=0

and

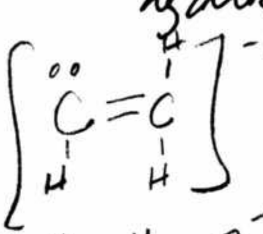


Factors are.
1. Electronegativity
2. Size
3. Geometry $sp < sp^2 < sp^3$

FC= 4-3-2 = -1
FC: 4-4=0

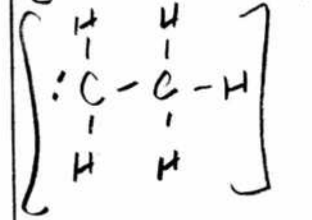
Electronegativity & size are not major factors for hydrocarbons. Move on to geometry.

more acidic sp^2

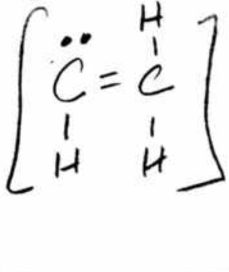


Geometry: left C: trigonal planar bent = sp^2
Right C: trigonal planar = sp^2

sp3



Left C: Trigonal planar bent
Right C: Tetrahedral sp^3



is more acidic. Good work

Ok, this is Correct!

Acids & Bases:

There are 3 factors we know of when evaluating strengths of acids & their conjugate bases.

1. Electronegativity
2. Atomic Radius (size trumps EN)
3. Geometry
   $sp < sp^2 < sp^3$

There are now three other things we are going to learn about:

1. The effect of nearby atoms
2. Resonance effects
3. pKA's & equilibrium predictions

Put these all together & you are going to have some very useful tools to evaluate acids & their conjugate bases.

We still have some work to do:

a very important summary page. Accomplishments to Date on Oregon - Ca Trip. ✕

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May 02 2015

We are in a much better place now.
We know how to approach & assess a molecule now.

1. Assess electronegativity, polarization & dipole moments
2. Assess bond type: Covalent, polar covalent & ionic
3. Conductivity & solubility estimates
4. Lewis structure (are just great for me!)
5. Formal charge determination
6. Geometry of the molecule & its relationship w/ hybridization sp sp^2 sp^3 esp.
7. Melting & boiling points estimates are coming
8. Lone pairs & lone electrons
9. Predicted properties, Avogadro geometric construction, ACD search, SBDS etc

10. A Big One - Acid Base Chemistry
    Factors: of conjugate base analysis
        1. Electronegativity
        2. Atomic Radius (size trumps EN, g. in %o)
        3. Geometry $sp < sp^2 < sp^3$
    To Do Factors:
        1. Effect of nearby atoms
        2. Resonance effects
        3. pKA's & equilibrium predictions

11. You have already predicted polymerization

12. This is all in addition to very insightful & accomplished IR spectral analysis (including identification of sub peaks, derivative & combination influences. & Creation of structural prototypes

Very
important
[illegible]

Page 70

Where we are going next:

1. The three remaining effects on acid-base chemistry that Org Chem WB wants to teach us

2. A re-analysis of the polymerization situation.

3. An examination of potential aldehyde & ketone relationships & reactions

4. Extensions into more detailed re analyses of the probability model eg blood, urine, protein, etc

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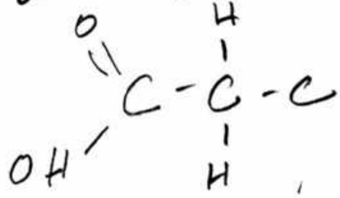
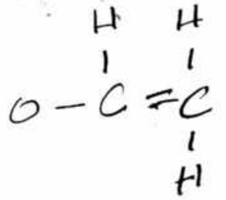
Note:

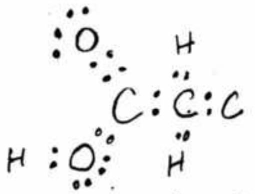
1. In geometry analyses, multiple bonds count as one

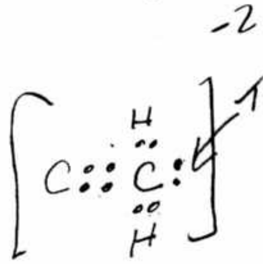
2. In formal charge analyses, each bond counts separately.

Let's look @ the polymerization process again.
Assume we have









-2

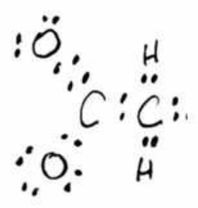
This lone pair is incredibly important!

C FC = 4 - 4 = 0
Geometry:
Bonds = 3 is
Trigonal planar = sp^2

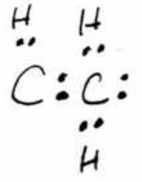
FC = 4 - 4 - 2 = -2
Geometry:
Bonds is 3
Trigonal planar sp^2

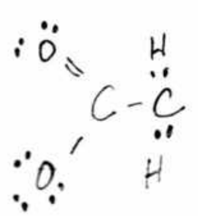
Top O FC = 6 - 2 - 4 = 0
Bot O FC = 6 - 2 - 4 = 0.

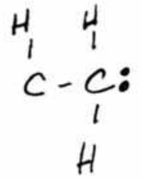
We see here that the O on top acts as a base. The H acts as an acid.
In alkenes, in polymerization, the double bond becomes a single bond. How & why?



I don't have it yet.







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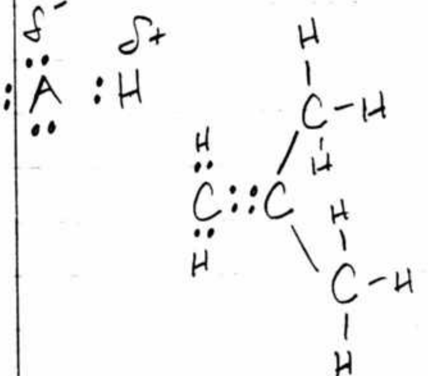
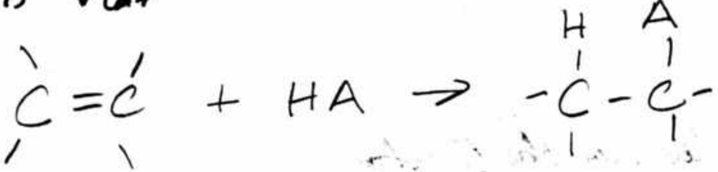
Lets look @ Org Chem EZ p69
Example of polymerization.



Now, we know the H is partially positively polarized because of the electronegativity of A.

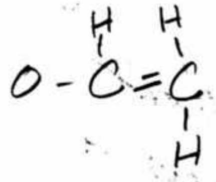
Another way that he shows the generalized reaction is that



Now, this seems much easier to understand.

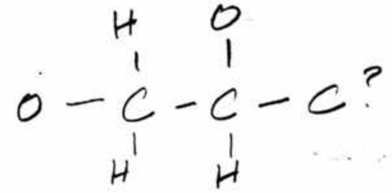
In our case, we have a terminal alkene of

Start with

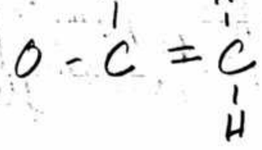


Since our HA is OH, we should get

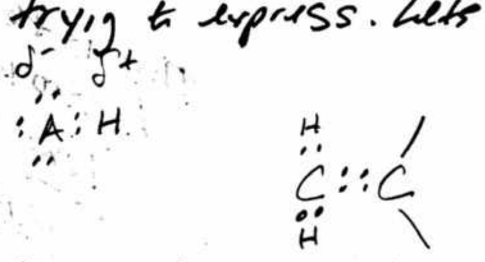
goes to



Notice the similarity of this to our original form of

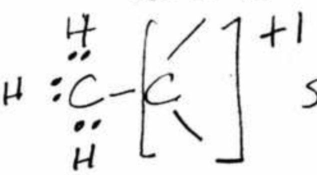


But I am not sure that this captures what he is trying to express. Lets go back to his example.



This is indeed our terminal alkene in a reversed form

Now what he says is that H^+ attracts electrons from the double bond & turns it into a single bond. He does not even care about the A! So it changes to



So this is looking for electrons. Guess where it gets them. Another terminal alkene!

FC=4-4=0

FC=4-3=(+1)

So any source of partially polarized hydrogen ions will suffice. from an acid.

Remember Oxygen can act as both an acid or a base apparently?

An Examination of OH Radical
OH

I know OH^- is a base

but what about OH? What is its Character

$$H\cdot \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \quad \Rightarrow \quad :\overset{\cdot\cdot}{\underset{\cdot}{O}}:H$$

This is the hydroxyl radical. Notice the lone electron!

$$FC = 6 - 1 - 5 = 0$$

So OH^- must be:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$$

$$FC = 6 - 1 - 6 = \boxed{-1} \quad = OH^-$$

This is the hydroxyl ion They are different

NaOH is a very strong base.

Oxygen normal state is 2 bonds

$$Na:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$$

The reason that this is acidic is because it dissociates into Na^+ + OH^-.

It seems to me that both OH & OH^- can act as bases since they both have excess electrons available.

But we also know that it has a partially positively charged hydrogen so it does seem as though it could act as an acid

vs the OH^- ion. An interesting situation. w/ fewer electrons available.
What if we had

$\ddot{\mathrm{O}}\!:\!\mathrm{H}$

$FC = 6 - 1 - 2 = +3$ Cannot be

We have learned the difference now between the OH radical & the OH^- ion. They both seem like they should be very reactive, but especially the OH ion.

What is the difference between the hydroxyl radical and an alcohol? I do not see any?

The lone electron would be the reason that OH radical would so much want to be a part of something else, like carbon, which it clearly can be. Think of what you really have

$\cdot\dot{\underset{\cdot}{\mathrm{C}}}\cdot \quad \cdot\ddot{\underset{\cdot}{\mathrm{O}}}\!: \quad \cdot\mathrm{H} \Rightarrow \cdot\dot{\mathrm{C}}\!:\!\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\!:\!\mathrm{H}$

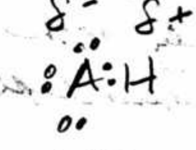
You see it? It wants to bond w/ something else and it does. If it was by itself it would be very reactive.

The OH^- ion, in contrast, is often dissociated and is what one definition of a base is.

May 03 2015

Today we still have a similar agenda. You're starting to see what is happening w/ terminal alkenes & polymerization. We want to review & re-expose this.

Ok, Back to Polymerization.
This is our situation:

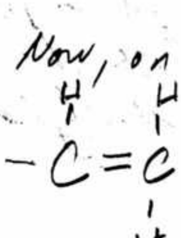


(This could easily be, and in our case it is Oxygen.)

An electronegative structure we do not care what it is composed of. O is a great example

So we actually have

Now, on the other end of the chain we have



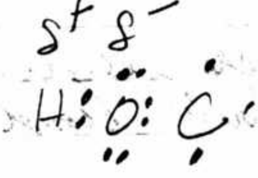
Now, he says the H$^{\delta+}$ attracts electrons from the double bond of carbon & turns it into a single bond.
Now if it breaks the bond to a single, what happens?

FC: 4 - 3 = $\boxed{+1}$!

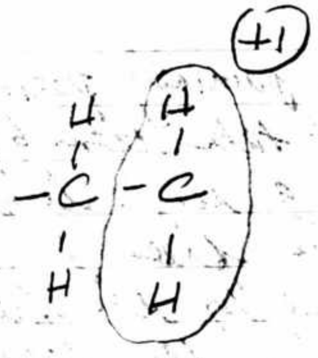
This is very intricately. The sequence seems to be

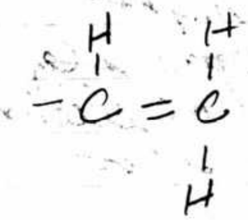
1. The partially positive hydrogen seeks electrons.
2. It takes them by changing the double bond to a single bond
3. The freed 2 electrons.
4. One of the free electrons ~~would~~ might stay with the left carbon and one electron might come from the hydrogen of at transfer intact?
5. Then you could form a CH bond on the lower left.
6. You still need another electron for valence on the right carbon.
7. Then the carbon want to form a new chain. NO NO NO. The right carbon is to maintain the charge of +1 so it want another electron.
8. So the double bond provide the electrons for a hydrogen proton to join.
9. The process repeats. Now we need to see how it repeats.

Poly meryation,
How does it repeat?
What do you now have available?



and now:



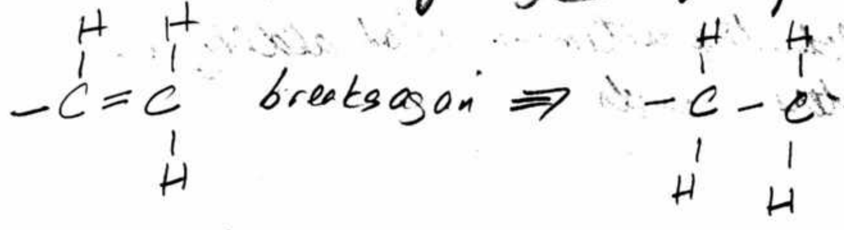


You have 3 parts.
1. partially polarized hydrogen atom
2. terminal alken that wants to go to a single bond
3. a charged alkane structure that is desperately seeks ~~electrons~~ an electron.

We have a hydrogen that is certainly seeks an electron.

But we have a ready source of elec with the C=C double bond.

1. So the polarized H it would love an electron
2. the double C breaks again and provide 2 electrons.



$$-\overset{H}{C}=\underset{H}{\overset{H}{C}} \xrightarrow{\text{breaks again}} -\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}$$

So this can happen repeatedly in parallel. Hundreds or millions of times simultaneously. So you have many charged sequences of alkenes that want to do nothing but bond w/ each other.

① The double C=C bond provides a ready source of electrons.

② The oxygen atom that was attached to the hydrogen also would seem to be a fantastic source of electrons.

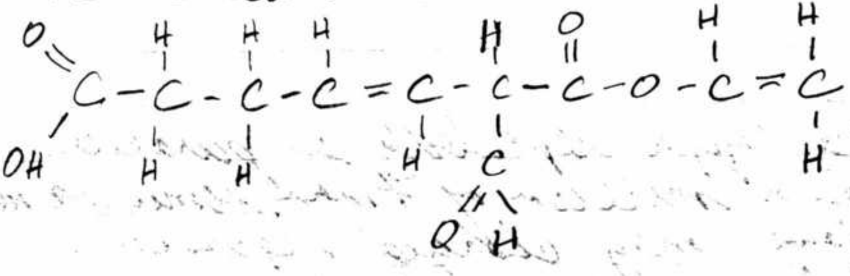
Looks to me like the process of polymerization is largely supported.

How do we get it started? Enzymes, Metals, Heat?

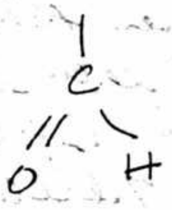
I think that we are better off now.

Do you see that you have to prospect at three different carbonyl groups here? Carboxylic acid
aldehyde
ester

Now lets transition to what aldehydes & esters can do.



Our topic of interest here is



What can they do?
So now we study
aldehydes p221 Org Chem EZ

They do not have partially positive hydrogens so they cannot be hydrogen bond donors.
This means they do not act as ~~bases~~ acids.
But it seems to me that the O can still act as an base.

C=O is polar, boiling points are higher than alkane

There appears to be a entire array of reactions that can occur w/ aldehydes.
One of the most important seems to be one with nucleophiles.

So what is a nucleophile?

It is a species that can donate an electron pair, per Elana relay in Washington!
Org Chem
Note: C=C bonds act as nucleophiles also p96 Murray

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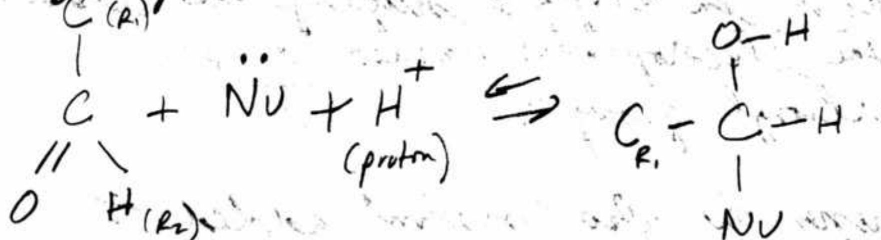
Now lets see how to interpret this :
First, from Spark Charts, this all correct :

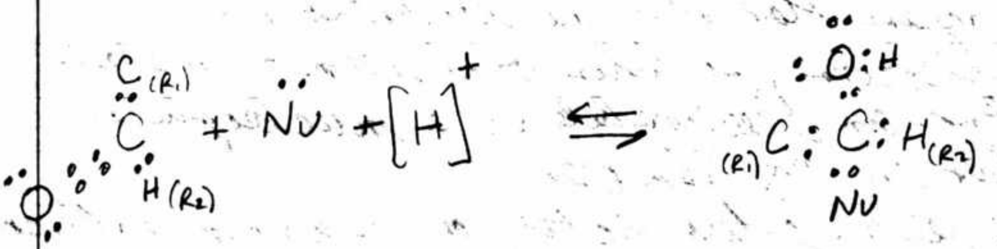
1. Nucleophiles are electron rich
2. Indeed there is a correlation between bases & nucleophiles, as we predicted.
3. Nucleophilicity increases as we go down a group in the periodic table.

Now on p224 we learn that a primary reaction of aldehydes is: NUCLEOPHILIC addition to the C=O group. Now how?



Spark Chart Org II Shows that this reaction is highly likely.

Guess who is electron rich? Transition Metals!
There is tremendous potential w/ aldehydes.



Before we go any further even w/ nucleophiles and aldehydes there is an oxidation statement that needs to be made.

In essence, you see $\ddot{\mathrm{Nu}}$ and H^+ add & change the double bond to single in the process. Nature does not generally seem to favor double bonds.

Murray sec 9.1 Org Chem says

"aldehydes are easily oxidized to yield carboxylic acids."

So this likely means something to us. but we also have Murray sec 9-5 saying

"the most common reaction of aldehydes and ketones is the nucleophilic addition reaction, in which a nucleophile adds to the electrophilic carbon of the carbonyl group".

Amines are also commonly added to aldehydes - this can easily involve amino acid interference.

Now, with metals, like Fe^{+2}, this means that they are deficient in electrons, so this would seem to make them an electrophile vs a nucleophile.
But in Org Chem EZ
We see an entire section on organometallics in combination w/ aldehydes so keep an open eye on that one.

Aldehydes are just full of opportunities.

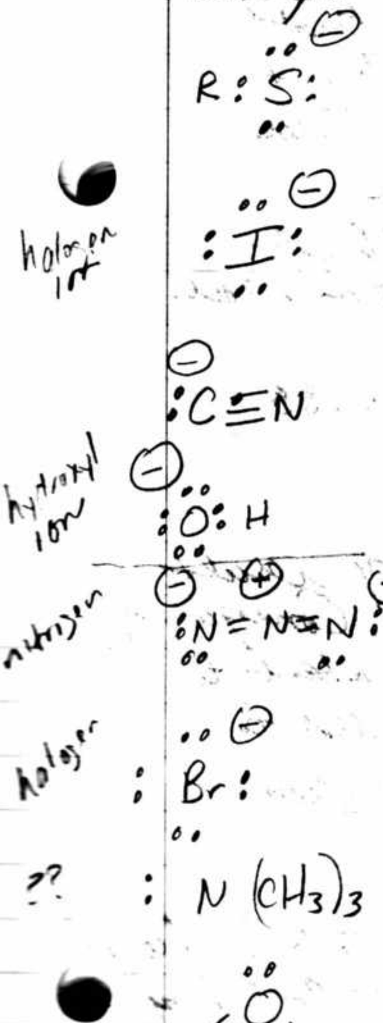
From Sparks Orgs II There is a table on nucleophiles.

Statement: ANY Species carrying an electron lone pair can act as a nucleophile.

That's big, isn't it?

1. There is some correlation between base & nucleophilicity
2. Nucleophilicity increases strength moving down w/in a group of the periodic table.

Also, there is a table.



More ~~Electrophilic~~ Nucleophilic

FC=6-1-6=-1

FC=7-8=-1

FC=4-3-2=-1

FC=6-1-6=-1

FC_{left}=5-2-4=-1

FC=7-8=-1

FC=5-1-4=0

LESS Nucleophilic

FC=6-2-4=0

Notice that the majority of these nucleophilic species are negatively charged ions. If something has a negative charge then it has an excess of electrons in addition to the fact that it may have had plenty of electrons already, like the halogen.

We are seeing a great deal of reactivity potential here with the aldehydes

1. With nucleophiles
2. with amines
3. with halogen
4. I believe with many bases in general
5. the hydroxyl ion
6. We need to see how metals enter the picture.

A metal like Fe^{+2} should have a deficiency of electrons so I am not sure how that qualifies yet. This does not seem to fit the electrophile definition. But on the other hand, don't transition metals have an abundance of electrons - eg up to 18 for valence activity? Need to work on this one more.

From Bruice Org Chem Sec 18.4 p 736
Listen to this:

"Few reactions in organic chemistry result in the formation of new C-C bonds. Consequently, those reactions that do are very important to synthetic organic chemists when they need to synthesize larger organic molecules from smaller molecules."

Continuing:
The addition of a carbon nucleophile to a carbonyl compound forms a ~~product with~~ new C-C bond forms a product w/ more carbon atoms than the starting material."

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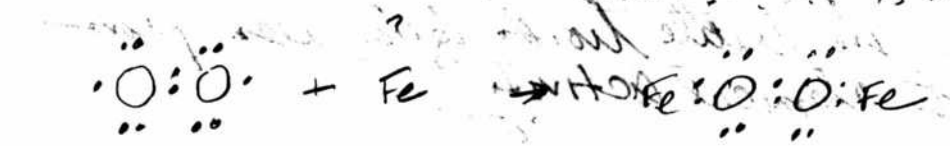
Our last group, at least for now of much interest in the lecture.

We also need to learn more about
transition metals
& organometallics

Lets play around with O_2 & Fe^{+2}

$O_2 + 2Fe \rightarrow 2\overset{+2}{Fe}\overset{-2}{O_2}$

??? Is this right?



Oxidation state has a very interesting & unexpected definition:

The charge that an ion has or an atom "appears" to have when the electrons are counted according to "arbitrarily accepted" rules.

1. Shared electrons by unlike atoms are are counted by the more electronegative atom

2. Electrons of like atoms are divided equally

It really is a tricky business, see p 259 EZ Chemistry

This is all quite strange.
It actually is strange:

This really is odd

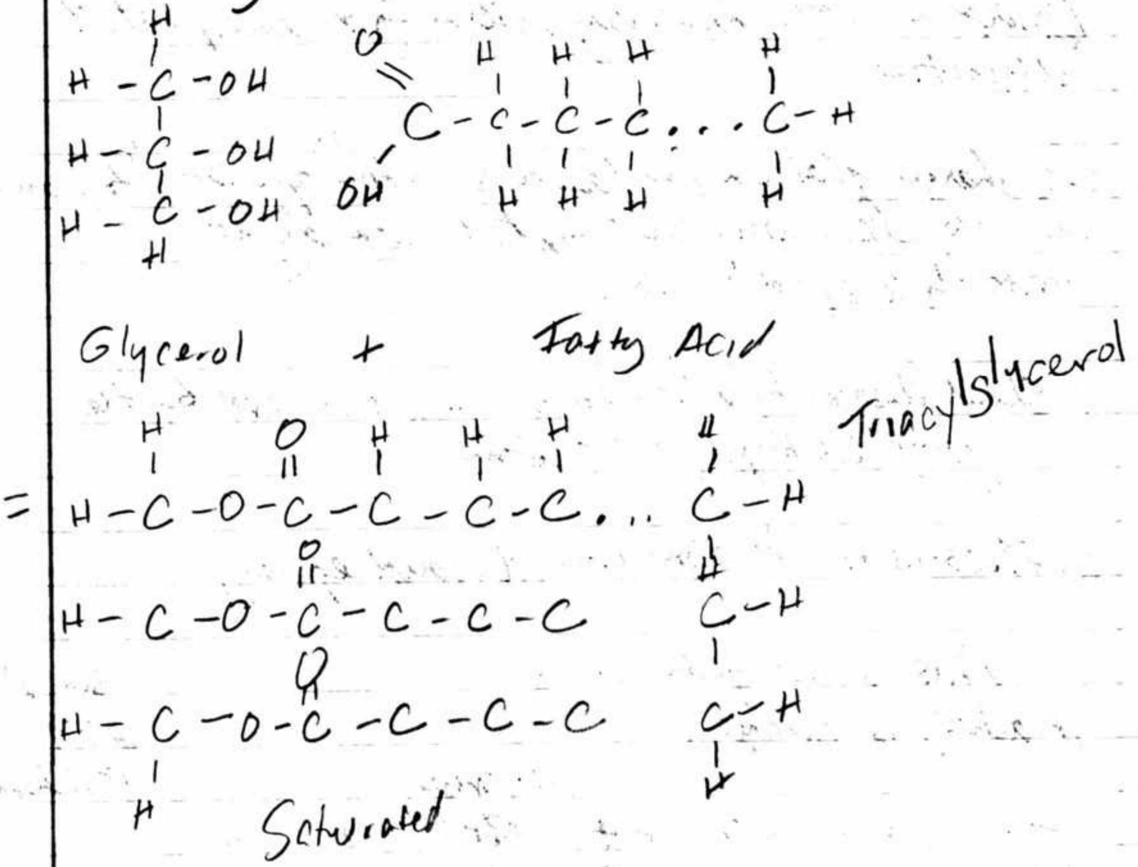
+1	+2	+3	+4	very strange +3	-2	-1
H, Na	Mg, Ca	B, Al	C	N	O	F

Ok, where are we now?

1. you understand the polymerization much better.
2. you see that the double bonds are a point of activity no matter where you go.
3. Aldehydes are especially prone to nucleophilic addition.
4. Esters are a carboxylic acid derivative (it seems to me that aldehydes are also but nobody said that yet)

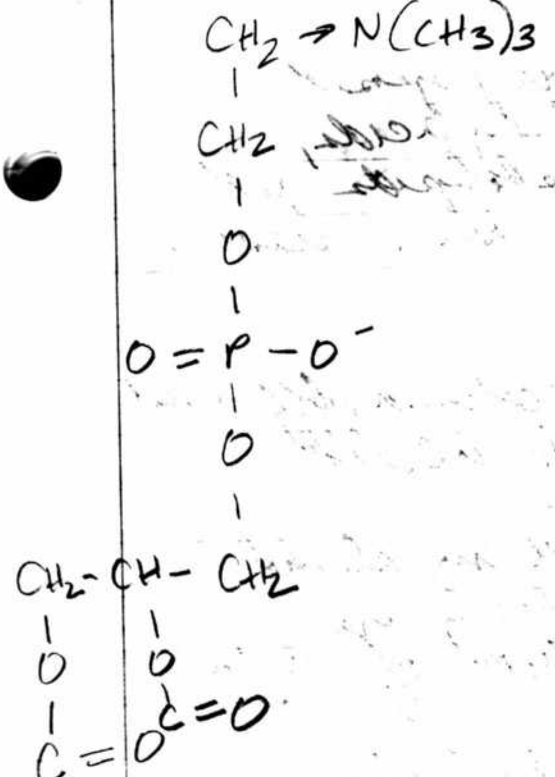
and the double bonds again seem prone to chemical activity.

A Fatty acid has the structure



Notice in a fat molecule that you no longer actually have a carboxylic acid. You lose it [illegible] to [illegible] complex that forms. And yet we have a strong carboxylic acid which indicate that technically it is not a fat molecule but that it is still a lipid.

The structure of a ~~phosphaloly~~ phospholipid is also its own story.



+
fatty
acid

~~[illegible]~~ steroids ~~also~~ do not seem to match.

These are a combination of aliphatic & ring structures (hydrocarbons) w/ an alcohol ~~attached~~.

Thus, so far no match w/ biological lipids.

Correction-

A carbonyl group is NOT the same as a carboxylic acid

CARBONYL: CARBOXYL

aldehydes
ketones

Carboxylic
acids

You have not ~~compared~~ compared your proposed structure w/ that of fatty acids, fat molecules, phospholipids and steroids & you do not have a close match @ this time.

You see significant modification a difference

1. You have carboxylic acids vs ester linkages
2. You also do not have any alcohol of a glycerol showing up.
3. You have indication of major conjugation
4. You have lots of double bonds
5. You have major departures such as vinyl alkene & aldehydes
6. [illegible] Steroid does not match either

Next, we seem to want to:

1. Take the next IR spectra study, eg urine, blood, etc protein?

2. Study Campbell - Biology - the big picture

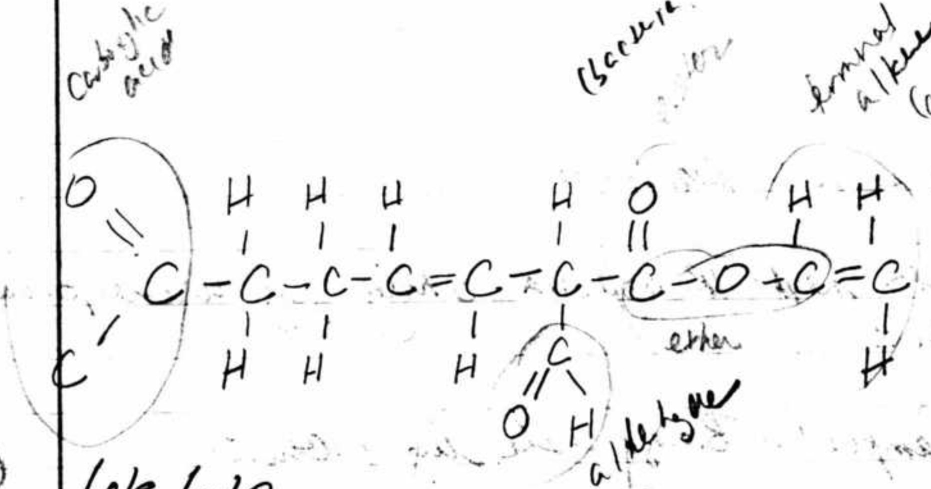
3. Find out if transition metal can be nucleophile.

Ok, I have figured out some of the issues affecting metal valences. Within the transition ~~metals~~ the 3d & 4S are very close in energy levels. This Combination leads to a max configuration of Uuo (#118) of $6d^{10}7s^{2}7p^{6}$ and since both S & d can be involved in reactions you see you can have the total of 18 electrons. And this is where the reference to 18 electrons came from.

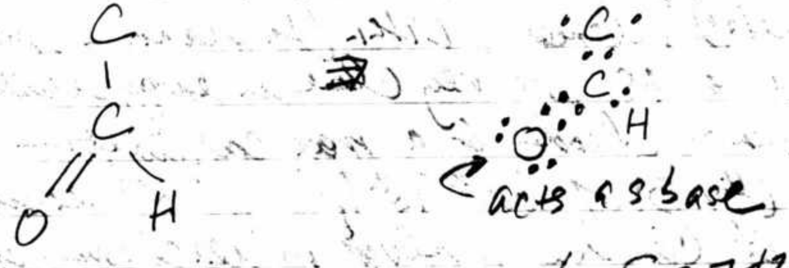
Now you can see that IRON is $3d^{6}4s^{2}$ And this gives a total of up to 8 electrons that can be involved. It is just circumstance that this matches the octet rule of 8, it is & can be otherwise w/ the other metals, eg ~~Mg~~ Cu is $3d^{10}4s^{1}$ = 11 total.

So Iron can vary from $\ddot{\text{Fe}}$ to $\overset{\cdot\cdot}{\underset{\cdot\cdot}{:\text{Fe}:}}$ and $[\text{Fe}]^{+2}$ $[\text{Fe}]^{+3}$ will strip off one of the d electrons. Now you see it.

*



Lets look @
aldehydes & transition metals like iron



Now what if we have $[Fe]^{+2}$ acts as a acid

looks to me like a set up.
I think we get

??

This looks like a perfect setup for the ferrous ion.

O formal charge : $6-4-0=+2$
This may not be normal @ all.
What about w/out Fe?
$FC=6-2-4=0$.

Proposed Scenario of Aldehyde Binding to Fe^{+2}

What about only one iron being added?

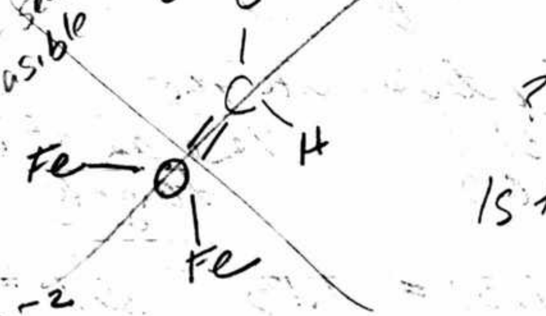
FC= 6-3-2 = +1 which is also not normal.

so we need to see if the structure is realistic or not.

So is this a feasible structure?

Does not seem feasible

???



???

Is this feasible ??

Forms 2 bonds

$\overset{+4}{Fe_2}\overset{-2}{O}$

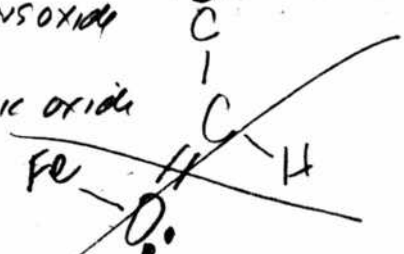
but if it was $\overset{+2}{Fe}\overset{-2}{O}$ this would work.

So maybe we could simply have

$\overset{+2}{Fe}\overset{-2}{O} = \varnothing$ ferrous oxide

$2\overset{+6}{Fe}\overset{-6}{O_3}$ ferric oxide

Not feasible



So is this feasible

FeO

is neutral wrt oxidation states

FC = 6-3-2 = +1

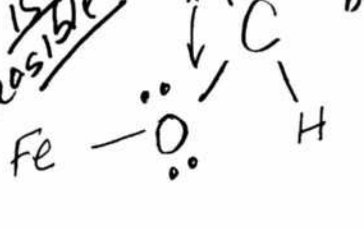
O forms two bonds

Oxygen forms normally two bonds, not three so.

Fe^{+2}

I think that this IS feasible

this bond is reduced to a single bond



FC Oequals

6-2-4 = Ø OK!

Great. looks very good!

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You may already have in your hands the mechanism to interfere with the growth after your hands.

1st Question: What is the ΔEN of Fe & O?

O = 3.44
Fe = 1.83
Δ = 1.61 Definitely Polar Covalent.

What would interfere with this
Mg = 1.31 These are the
Ca = 1.00 targets.

Mg: 3.44 - 1.31 = 2.13 30.6% ionic
Ca = 3.44 - 1.00 = 2.44 32% ionic

Fe & O: 27.2%

Fe: 3.44 - 1.83 = 1.61

May 04 2015 Monday Smith River

1. A strategy has already been developed from electronegativity of Mg^{+2} & Ca^{+2} to interfere w/ iron absorption.

2. Need to start understanding citric acid & VitC response. Valerian? urine, hormone influence?

3. Thinkwell is superb and you have missed much of it. Molecular weight determination is amazing - Δ Boiling Point & Osmosis?

4. Need to take on another spectrum w/ probability model - urine or blood?

5. Verify transition metal response w/ aldehydes

6. Method to interfere w/ polymerization?

7. Watch Thinkwell also! - Campbell chapter also!

Thinkwell course so on.

Bacteria - siderophore mentioned again

Dist 9
Coordination Complexes

Colors of Transition Metals

Harmon: separation of d orbitals w.r.t. ligands

some other source says degree of conjugation

Which is it? One and/or both?

Spectrochemical Series (of Ligands)

Repulsion causes d orbitals to split
into different energy levels

C N O tend to form multiple bonds
but not much else below it in
the periodic table is.

Let's return to IR Spec Interpretation

4. Structure Development:

Main Tools are

1. IR Spec
2. Chem Toolbox
3. Koji
4. Prob. Spreadsheet
5. Pavia if need be
6. IR Quick & Easy References!
7. IR Explainer - is actually useful

1. We start with major peak @ 3335.

We have lots of choices here

IRSpec | Amine 3300-3500

Alcohol 3200-3650

But before we go further, what we really see is that there are subpeaks.

What we really have is a major peak from 3550 - 3080

Our best fit here is an amine

		Meas	$\bar{X}$	Δ	Theoretical	$\bar{X}$
IRSpec	Amine	3080-3550	3315	185	3000-4000	3500
	OH Alcohol	3080-3550		110	3200-3650	3425
	Amine	~~3300-3500~~		85	3300-3500	3400

-1 TB | And so you see you are missing the big picture again. The real, 1st primary peak is huge, grab this before you try to break it down. This is from 2200-3550

		Meas	*	$\bar{X}$	Δ	Theoretical	X
TB	COOH	2200-3550		2875		2500-3300	2900
IRSpec						2500-3100	2800
IRSpec	N-H Amine (NH_4^+ ion)	2200-3550 ~~2400-~~				2400-3200	2800

So two candidates show up with the broadest peak

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Ok, we have a COOH in along w/ an amine prospect but low score for each. We know from Quick & Easy that indeed it is a COOH but we should not jump to it. So far, COOH wins.

Also, the lower score are telling you that you have some kind of issue remaining, most likely Combination effects.

Now let's look at slope break.
Something is happening @ 3080 w/ a slope break.

Before we go on, however, we can use Koji as a source for 2200 – 3550
What we see in Koji is a likely overlap between COOH & ammonium compounds
Ok, on to the slope break.

2200 – 3080

Now, we have clearly picked up the amine from the slope break @ 3080. The COOH is still weaker than desired but nothing competes with it.

We ~~should probably go for the carbonyl groups next~~
Lets pick up the peaks of the major COOH peak.

We have sidepeaks @ 3460, 3350 & 3190.

IRSpec Before we go onto this, we can also ~~incorp~~ incorporate IR explainer into the toolset.

First, to pick the center of the broad COOH @ an average was very incorrect. It should have been in the center of the observed main peak @ ~ 3300, not 2875.

Now, we notice something. Our COOH ~~determinatio~~ is low & weak because this peak is way off. The peak of a carboxylic should be at ~2970. Ours is @ 3330. So our main peak is clearly not a carboxyl. ~~however~~. However it does look to be an OH or amine, just as IR explainer said.

IR Explainer Gives OH or N-H (could easily be both.

So this was very interesting. IR Explainer has picked up an alcohol or phenol that you have completely missed to date and yet it is a very strong candidate.

Which already picks up NH - OH - COOH Combination.

You missed a major feature. You also have an OH Candidate along w/ the amines.

3350
Ok now go for peaks @ 3460, ~~3350~~, & 3190

IR Explainer is only very broad. info. It is not very specific.
these are subpeaks & tight range

IRSpec Amine is nr. Closest.

IR Explainer is mn for major groups
IR Spec] are for detail.
ChemTB]
Koji is for backup & clarification

~~IR Ex~~ Chem TB gave superb amide match on all 3 sub peaks.

We have amine, amide, OH & COOH now.

An amide is not at all an amine!!!
Amides have a Carbonyl.

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Ok, on we go to the peak @ 1650.

Our broad peak is from 1500 - 1735

We appear to have a combination of:

aldehydes, OR ketones OR COOH
combined w/ amines
Combined w/ nitro compounds.
Phenyl Ring is also a possibility
There are even some aromatic rings in here.

What is a nitro compound? NO_2 & such
So there are many calculations here.
1617 is our center 1500 - 1735
IR Spec: lots of choices

Amine	~~N-H primary~~	~~1560 - 1640 *~~	~~Strong~~	✓
~~Alkene~~	~~C=C~~	~~1620 - 1680~~		
	~~Benzene Ring~~	~~1450 - 1600~~	~~weak~~	
Carbonyl	~~C=O~~	~~1610 - 1780 *~~	~~Strong~~	
	Benzene Ring	1660 - 2000	weak	

Chem Toolbox 1~~680~~ -1

~~COOH~~	~~1600-1740 *~~	
~~Amine~~	~~1550 - 1650 *~~	~~NH_2~~
~~Ketone~~	~~1580 - 1650~~	~~C=C stretch~~
~~Amide~~	~~1530 - 1650 *~~	
~~Alkene~~	~~1630 - 1680~~	~~C=C stretch~~

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Our current situation is

Carboxylic Acid	78%
Carbonyl	45%
Ketone	68%
Amine	100%
Amide	100%
Alkene	87%
Benzene Ring	65%
Alcohol	71%

Now Sort:

Amine	100%
Amide	100%
Alkene	87%
Carboxylic Acid	78%
Alcohol	71%
Ketone	68%
Benzene Ring	65%

at end of Carbonyl peak w/out sub peaks

Next we move on to the sp peaks of the carbonyl
1615
1665

1615: TB: Arene 1590-1630 good
C=C in ring.
IR spec does not come out as strong a metal.

IR explain suggests aromatic ring, & amines. not favorable
1590-1630 good 1550-1650 Δ=100
Let's look @ 1665: TB:
Alkene 1630-1680 good
Ketone 1665-1705 Unsaturated

Now we have:

COOH	78%
Carbonyl	45%
Ketone	88%
Amine	100%
Amide	100%
Alkene	99%
Benzene Ring	99%
Alcohol	71%

or

Amine	100%
Amide	100%
Alkene	99%
Benzene Ring	99%
Ketone	88%
COOH	78%
Alcohol	71%
Carbonyl	45%

It is firming up.

Now we pick up 1450 nice & Strong.
Range is 1400 - 1500.

IR Explain
Alkanes
~~Aromatic Ring 1500-1510~~

~~TB: Alkane 1450-1470 CH_2~~
~~IRSpec Alkane 1440 Strong methylene~~

Koji supports this same approach.
~~Koji Alkane 1400-1410~~
~~Aromatics 1450 - 1600~~

Now we have

		to	
COOH	78%	Amine	100%
Carbonyl	45%	Amide	100%
Ketone	88%	Alkane	100%
Amine	100%	Aromatic	100%
Amide	100%	Alkene	99%
Alkane	100%	Ketone	88%
Alkene	99%	COOH	78%
Aromatic	100%	Alcohol	71%
OH Alcohol	71%	Carbonyl	45%

Next we go to 1135 range 1000-1200

1135 Range 1000 - 1200 Finger print region
Notice that it is not symmetrical. But neither is COOH.

IR Explainer:
Amines, alkyl halides, alcohols, COOH, Esters

TB: ~~Alcohol 1030 - 1100 good~~ NOT DONE ok good
~~Amine 1000 - 1250 good~~ good

IR Spec Alkyl halide 1100-1200 no Support
~~Amine 1020-1230~~ good
Ester 1100-1300 not so good
ok NOT DONE ~~Alcohol 1150-1200~~
ok NOT DONE ~~Alcohol 1100 Strong~~
ok NOT DONE ~~Alcohol 1200 Strong~~

Koji alcohol, ~~phenol~~ 1000 - 1200 T5b good
~~Aliphatic Amines 1030-1230 T7~~ superb
~~Ketones 1050 - 1300 T8~~
possible Thioketones 1040 - 1200 T11

It appears to me to be a combination
of alcohols & amines.

Next we have some minor activity @
1325 IR explainer Amines, alkyl halide, Nitro
TB: Sulfone S=O 1300 - 1350
~~Nitro N=O 1320 - 1360~~
IR Spec Nitro 1350 N-O Aromatic
IR Explainer NO_2 Symmetrical Stretch

1240 IR explainer

~~you~~ .

You saw Nitro in IR explainer NO_2
IR explainer has Nitro ~~1500-1660~~
and ~~1260-1390~~
These can not be ignored.

This was very interesting. You picked up an unexpected Nitro group from 4 sources to give a Pr of 79%.

Now lets go to 1240.
IR Explain C-F, C-N or C-O
JB: No good match
1220-1200 IR Spec C-O Ether C-O Aromatic

~~C-H Alkane @ 1260~~
~~C-O Carboxylic Acid 1250-1300~~

Next is 925, a then 600

Now we have

COOH	89%	50	Amine	100%
Carbonyl	45%		Amide	100%
Ketone	88%		Benzine	100%
Amine	100%		Alkene	99%
Amide	100%		Alkane	94%
Alkane	94%		COOH	89%
~~Alkene~~			Ketone	88%
Alkene	99%		Alcohol	79%
Benzene	100%		Nitro	79%
Alcohol	79%		Carbonyl	45%
Nitro	79%			

The number & complexity of groups does indicate the possibility of multiple compounds

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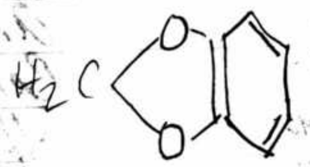
925

IR Explain says alkenes, but then says C-H

TB 930-960 Oxime N-O

IR Spec alkene $=C-H_2$ 900
Benzene Ring (meta distributed) 860-900

Koji 950-970 Aliphatic N oxides
925 methylene dioxy



This becomes more difficult to interpret,
Some overlap w/ others, NO is
probably the strongest.
but you see the set
alkenes
aromatics
N-O
and then a stray from Koji

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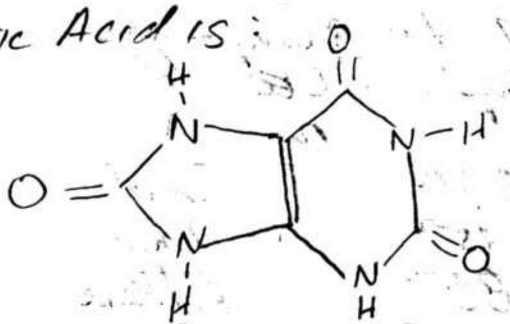
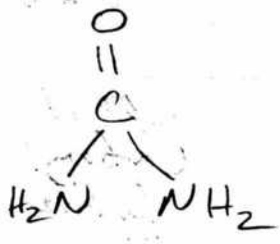
[redacted]

Uric Acid is:



Urea is



Lastly, we have something happening ≤ 600

IR Explainer says this is alkyl halide (actually Br)
~~a alkynes maybe.~~ Nothing else given.

TB: 550-700 C-Br also
600-700 alkyne
550-710 Thiol C-S

IR Spec 500-600 C-Br
600-800 C-Cl

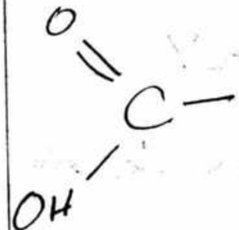
Not really much likely to be a competitor besides C-Br.

Therefore a summary of the groups for the urine sample [redacted] is

COOH	89%
Carbonyl	45%
Ketone	88%
Amine	100%
Amide	100%
Alkane	94%
Alkene	~~100~~ 99%
Benzene	100
Alcohol	79%
Nitro	79%
Alkyl Halide	50%

Amide	100%
Amine	100
~~Alkene~~	~~99~~
Benzene	100
Alkene	99
Alkane	94
COOH	89
Ketone	88
Alcohol	79
Nitro	79
Alkyl Halide	50
Carbonyl	45%
Ether	63%?

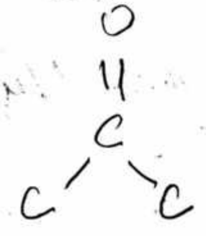
there is a lot of activity



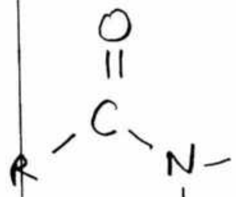
COOH
89%

① C=O

Carbonyl
45%

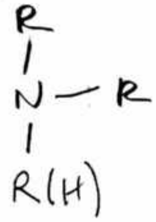


Ketone 88%

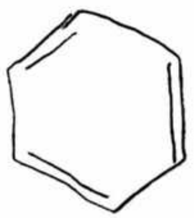


Amide
100%

①



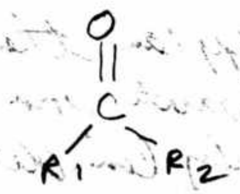
Amine
100%



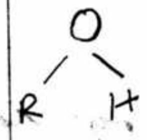
Benzene
100%

$C-H$
Alkane
94%

$C=H$
Alkine
99%



Ketone
88%



Alcohol
79%

$N-O$ (?)
Nitro (?)
79%

$C=O$
Carbonyl
45%

$C-Br$.
Alkyl Halide
50%

Urea certainly fits.

Urea

Carbonyl-amine

~~Note that urea meets the definition of a ketone.~~

The definition of a ketone is changing here - Sparks is very questionable

The definitions vary depending upon what you want to consider. The functional group is more specific. There is a "General Formula" that truly is more general

I am seeing that the definitions of functional groups actually vary.

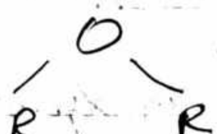
This points out the importance of IR Assignments to a particular type of bond. Your work must do this now

It appears then, therefore that you need to separate your bond types before you actually can determine probabilities. They can increase the complexity of the work but the work should be more accurate a a result.

You actually need to go through each group now:

As we are working through this we actually see the distinct possibility of an ether from the 1240 peak. Notice after it is an aromatic so that is interesting.
Listed as C-O aromatic

An ether is:



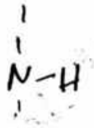
Our adjustment now is:

COOH	89%
Carbonyl	45%
Ketone	96%
NH_4^+	93%
N-H or NH_2	95%
C-N	68%
N-H	100%
CH_2, CH_3	94%
C=C	99%
Aromatic	100%
Alcohol	79%
NO_2, N=O, NO	79%
Alkyl Halide	50%
Ether	63%

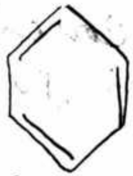
So:

Amide, Amine	
✓ N-H	100%
✓ Aromatic	100%
✓ C=C	99%
✓ Ketone	96%
✓ N-H, NH_2	95%
CH_2, CH_3	94%
NH_4^+	93%
COOH	89%
Alcohol	79%
NO_2, N=O, NO	79%
C-N	68%
Ether	63%
Alkyl Halide	50%
Carbonyl	45%

So the Urine Groups are [redacted] Urine Analysis



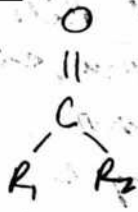
Amine
100%



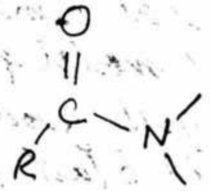
Aromatic
100%

C=C

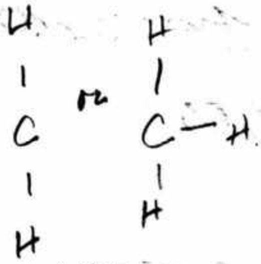
Alkene
99%



Ketone
96%

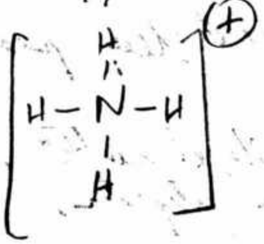


Amide
100%



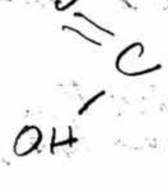
alkanes

Alkanes



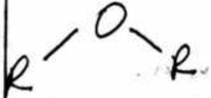
Ammonium Ion

Amm. Ion



Carboxylic acid

Carboxylic Acid



Ether
63%

C-Br

Alkyl Halide
50%

C=O

Carbonyl
45%

Uric Acid
Ammonia
Aromatic & Halogens
Ketones

This is a very Marvelous & Concentrated analysis of [redacted] urine taken, incidentally @ post session illness. It shows the presence of urea, uric acid, ammonia, ketone & possibly the addition of a halide group. The latter 2 are each potentially problematic & indication of metabolic stress.

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You have made tremendous progress here. Your model of your source cross correlation are quite good now. We will now go back to the blood sample

First, the big picture.
We have an extremely broad deep peak from 3600 - 2400.
But notice there is a slopebreak @ 2680.
We also have 2 major subpeaks.

Our first major peak looks to be @ 3280.

It goes to 3670 on left.
Δ = 420
3250 - 420 = 2830
We therefore believe that the first major peak runs from app. 2830 - 3670.
Midpoint = 3250.

It Explains: 3670 3250 2830

Our best match seems to be a monomeric alcohol or phenol ~3630 to 3170

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If you see what happens, the slope breaks @ 3100 so something happens at this point.

Our adjusted range is therefore 3670 - 3100. With peak @ 3250.

Now a graphical slope analysis indicates that the first peak ends @ approx 2800.

So our first range is 3670 2800
3250

vs theoretical
for IR explanation ~~3670~~ ~~2850~~
3630 3170
3400
theoretical

There's more unusual.
We definitely have
contamination effects

What you see happening are two major peaks that both overlap. @ 3250 and 2925.
Let's find these first.

3200 - 3650 alcohol O-H
3000 - 4000 Amine N-H
3300 Alkyne $C\equiv C-H$

2400-3200 Amine N-H NH_4^+
2500 - 3100 Carboxylic Acid O-H
2925 Alkane methylene

So already you are seeing the potential for overlap of ~~these~~ major groups already

alcohols
amines
a carboxylic acid

w/ peaks of alkyne C≡C
and alkane (methylene).

A Big question is, what functional groups are within blood?

You have found your 2 sources
printout from net: Spectroscopic techniques in the study of human tissue and their Components. Part 1 Spectroscopy. (Janis)

And your spectroscopy textbook in life & biomedical sciences.

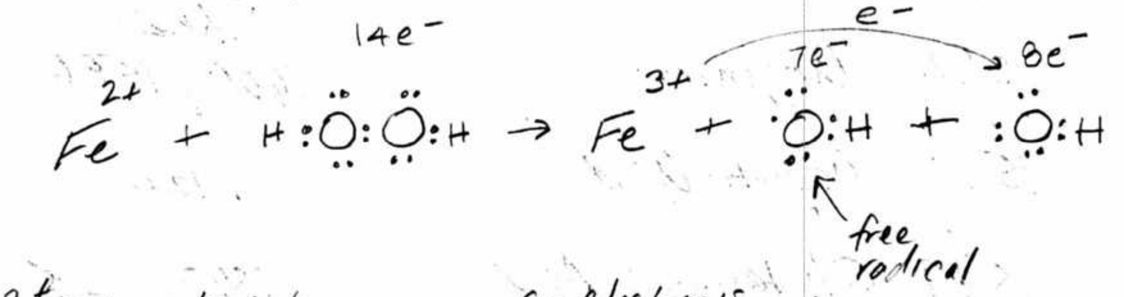
Janis paper gives 3300 of NH & OH
in water molecules, proteins, polysaccharides
& Carbohydrates

2935 ~~CH~~ a CH_2 but he assigns as
long chain of fatty acids and phospholipids

These assignments seem like we
have a real match.

Guess what:
You are finally in a position to understand free radical production

$Fe^{+2} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + \bar{O}H^-$



2+ means that it has lost two electrons. These are the two S electrons so there are none

an electron is taken from the d shell to accomplish this

The IR Spec of the blood CEE is already very interesting. There are, according to Janus' paper, 4 zones of erythrocyte activity.

1. 3300 - 2930
2. 1606 - 1518
3. 1230
4. 1085

Guess what, you have them all plus some additional activity starting @ 3650 and in the zone of 600 or so. (Remember your urine @ 600 ?) (Halogen or alkenes ?)

The Barbara ~~Stua~~ Stuart book on IR is quite valuable. Biomolecules are covered in detail. It looks to me like she did the work.

Life Sciences IR book has amino acids @ p279: Proposed & Stated

		Stuart
1592	Arginine	1608, 1586
1510	Aspartic Acid	1720
1541	Glutaminic Acid	1560, 1415
1512	Tyrosine	1600, 1450

Notice that they do not agree.
The creates quite the quandry, doesn't it?

There is major disruption of the proteins in the blood w/ the introduction of the CDB into the blood.

Notice also that urea is expected to be in the blood.

We have 3 sources for IR Biological Study
1. Janes paper
2. Stuart textbook, short but powerful
3. Theophilus Collection.

We are seeing that we are right on track w/ our IR analysis & that derivative use was indeed powerful. We also have a difference technique that we will be using. Your spreadsheet is perfection.
So back to blood analysis, go where it goes.

[redacted]

We do indeed see 2 major combined peaks.

3670 - 2850

3280 - 2690

We have a slope break @ 2690.
So 3670-2850
IR Explain
~~3600~~ - 3670 - 3200 is OH
3000 - 2500 is COOH
3500 - 3300 is amines
We also have ~~a~~ hydrocarbons in this region.

So now look @ subpeaks also.
3250
2920

So we now have:

OH 99%
Amine 77%
Amide 94%
Alkane 100%
C≡H 85%
COOH 97%

This compares quite well w/ James
He has:
NH
OH
CH
COOH (fatty acids)

Very good.

Now because of the broad peak you have some question about the prospect for a carbonyl but notice that we may or may not have that. We do, however, have a very sharp decline @ 1700 taking place so indeed we may have a carbonyl. The broad peak extending to 2000 certainly indicates this prospect.

The Quick & Correctly does indeed indicate a COOH, nothing else seems to be like it. Even the disturbance @ 2650 is in line w/ the Carbon COOH example. It says to me that we have it.

And this actually matches, as he even says that we have fatty acids in the [illegible].

3800 - 2200 COOH quick & easy
2910 COOH peak

We have 3650- 2200
slope break @ 2200
our peak is @ 2925

[redacted]

We next have scaled down our model to max 95% confidence. So now we have

OH	94%
N-H Amine	~~94%~~ 73%
N-H Amide	89%
CH Alkane	95%
C≡C-H	81%
COOH	92%.

so Ranked:

C-H alkane	95%
OH	94%
COOH	92%
N-H Amide	89%
C≡C-H	81%
N-H Amine	73%

This looks superb to me.

Next we notice the activity @ (slope break)

2390 - 2320 IRSpec C≡N, C≡C, N-H(NH_4^+)

and 2190 - 2100 IRSpec C-N, C≡C, C≡N

Keep the above in mind as we go ahead. Something certainly did happen here.

Now we will go ahead w/ major activity from 1770 - 900.

We start with
1770-1660 large, smooth dip, this is Carbonyl!
IRSpec 1780-1670 Carbonyl. (C=O)
We may also have ester (C=O) or ketones (C=O)

Ramifications are coming to light here:
1. Polymerization
2. Free radical reaction
3. Fe^{+2} reaction w/ COOH is now proposed.

A switch in topic here.

We now have Murray's Org Chem Book in print form (India version!)

He has a fantastic chapter on how organic reactions take place, bond breaking, electron movement. Superb presentation

In it, he has an example of an alkene radical reaction that definitely catches our interest.

First, we have already seen with respect to a terminal alkene, that polymerization is likely to occur in combination with an acid.

But now we also see (p 113) that also with a terminal alkene that a free radical reaction can also occur and this also has important (potentially) implications of setting off a major reaction or a chain reaction or an important reaction.

So w/ terminal alkenes we already see:

8. Prop. CD Shaped Structure

Ramifications coming to light already alkene

1. Polymerization
2. Free radical reaction

are both likely to be important.

3. A proposed reaction of Fe^{+2} w/ ~~acid COOH~~ aldehyde has also been developed.
4. Disturbance of Blood Proteins
5. Genetic Origin - Domain Level
6. Vit C Mechanisms
7. Polymer Applications

(Elements on the slant line, even on right side of periodic table, can react as polar, eg C-S and C-I bonds)!

Polarization More Realistically & Comprehensively Discussed.

Polarization is not determined just by electronegativity.

It is also affected by atom size and the number & distribution of electrons (ie, electron configuration).

A good example is w/ the S-O bond.
If we think in terms of electronegativity alone we have
$\Delta EN = 3.44 - 2.58 = 0.76$
which is very borderline as a polar covalent bond.

~~But~~ And it even suggests that the attraction is from the oxygen side.

But IN FACT, sulfur is <u>more</u> polarizable than oxygen because of

1. increased atom size
2. more electrons, less tightly held

(look @ electronic configuration).

I do not think that this would ever have been anticipated without Murray making this point. In the end <u>Carbon - Sulfur</u> bonds do react in a polar fashion.

Same w.r.t. to Chlorine & Iodine. $\Delta EN = 3.16 - 2.66 = 0.50$ but A.R. of I is > Cl w/ more electrons so <u>Carbon - Iodine</u> bonds react as if polar!

THE SEVEN STEP PLAN

The Big Picture as of today

May 10 I believe 2015

What are the parts that are starting to come together now?

1. An IR spectrum (the better it is, the better the results can be)

2. Skill @ interpretation of IR spectra, along w/ a probability model for same
Note that you are ultimately interested in the assignment of bond types, not just functional groups involved.

3. Structural development to the degree possible (Avagadro, ACD ChemSketch, Search, SOBS)

4. Comparison of both the spectra & the structure with available reference data.

5. Identification of the most probable organic chemical reactions that are likely to take place

6. A true understanding of the what, why & how of these same chemical reactions according to Murray

7. With this understanding, a development of mitigation strategies to disrupt or interfere, & elimination in the harmful chemical mechanisms.

Page 123

Today
(loves electrons)
1. Let's work through the electrophile and nucleophile
(electron poor) (electron rich)
(electron deficient)

problem in Murray - India p117.

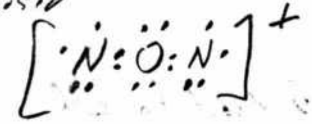
2. Then lets understand the polar reaction examples on p110. This is the most common type of organic reaction to take place

3. Let's go on to [redacted] blood IR spectra ~~interpretation~~. You are doing well & corresponding w/ Janus paper.

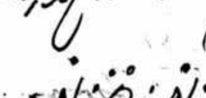
Starting with #1 for today:

NO_2^+

Proposed



Now, if it has a positive charge, one electron is taken away.
(Nitrogen is less electronegative than O.

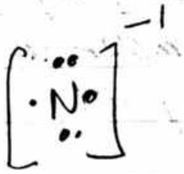


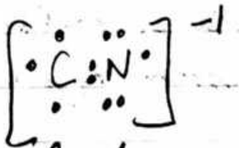
Now, is this an electrophile or nucleophile?
I say nucleophile, look @ all the electrons.
But it seems to me to say that N is an electrophile here and that O is a nucleophile. What does Murray say?

He simplified it by saying because it has a pos charge, it seeks an electron. This makes it an electrophile. I think my discussion is valid also though

Continuing:

CN^-

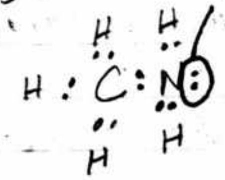


It also has a negative charge, so in this case it wants to give up an electron (toward a nucleus). This would make it a nucleophile

By my thinking, the N has almost a complete octet, and carbon is still seeking theirs. The charge approach (which is a net overall view of the situation) is a heck of a lot more straightforward!

CH_3NH_2

you failed to notice these!



Octet rule is satisfied by all participants.

No formal charge exists

~~There are the free electrons.~~ WRONG!

~~In general I would say neither electrophile or nucleophile however N is more EN and therefore slightly more electrophilic than carbon is~~

WRONG!

C: FC = 4-4-0 = 0

N FC = 5-3-2 = 0

IT IS NUCLEOPHILIC because it has a lone pair to offer on the Nitrogen!!!! You missed what you carefully identified and revealed as a primary mechanism!

No of bonds formed is what it takes to reach the noble gas configuration.

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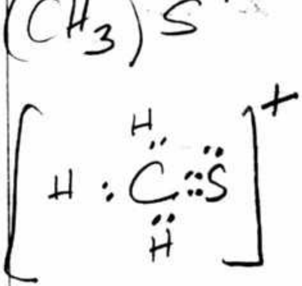
Sulfur should be forming 2 bonds.

$(CH_3)S^+$



S has how many valence electrons? 6?
How many bonds does sulfur form? (should be 2)
Why?

Seems to me it has ~~two~~ one lone pair available. Seems to me that this would make it an ~~electrophile~~ nucleophile.

~~But it also has a positive charge, meaning that it would like an electron, meaning an electrophile. But I think that the nucleophile wins out because of two lone pairs available vs seeking a single electron.~~

NOT TRUE !!

Straightforward example again.

A charge on the molecule appears to dominate all. Positive charge says it wants an ~~ebt~~ electron & that is that. It is an electrophile no ands ifs or buts

It was very good to do these problems, you see your weaknesses identified.

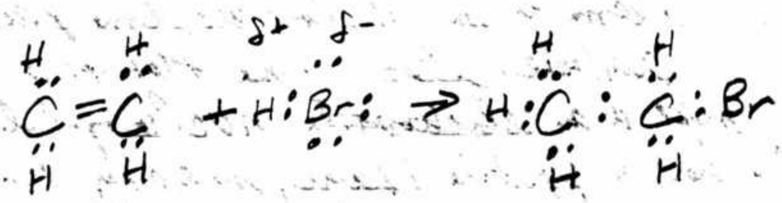
Now we are to go to p118 and work the polar example through since it is the mainstay of organic reactions

Remember Bonds; Electrophiles & Nucleophiles (and Polarity)

electrophile - electron rich
nucleophile - electron deficient.

The polar reaction example to be used as a master template is:

$C_2H_4 + HBr \rightarrow C_2H_5Br$ (a join reaction)



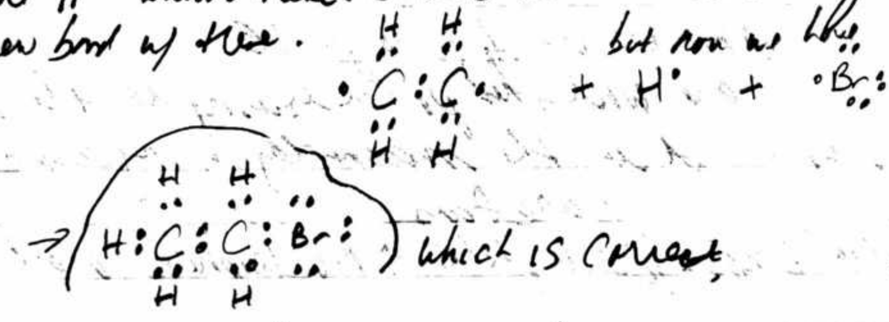
So, what happens is the question.

Lets start w/ polarity. CH_4 is not polar at all.
HBr is ~~highly~~ mildly polar w/ ΔEN's 2.96 - 2.20 = 0.76. So it would likely want to do something.
Now lets look @ electrophiles & nucleophiles.
The formal charge on each is 0.

Next we see that we have a double C=C bond. ~~[illegible]~~ an. This subject to attack as it is a rich source of electrons. The $H^{\delta+}$ is seeking those electrons. So the double bond can break providing a pair of electrons.

plus two free electrons.

The $H^{\delta+}$ wants these. So we should be able to form a new bond w/ these.



but now we have

Which is correct

Sequence of Understanding & Visualization 6.5?

*
1. Lewis dot
2. VSPR geometry
3. Hybridization to match the geometry.

See p112.

Now lets read the text description & all of use have to interpretation correct and then we will progress to an arrow depiction.

Is it symmetrical or non symmetrical (polar should be non symmetrical) bond breaking? p112

So first question I see.
Why is a double bond always a pi bond? answer: one σ and one is π
Why can it never be a sigma bond or two sigma bonds?
p 417 & 418 in Zumdahl Chemistry is going to teach us why we have σ & π bonds available.

OK now we understand hybridization much better. We used Zumdahl (p 414) which caused me some confusion as you see and also Chem for the Utterly Confused p 106 and this actually did seem to help matters.

You see now that the logical progression to follow in terms of understanding the geometry of bonding is

1. Lewis dot first
2. Then VSPR theory does give you the geometry
3. Then work in hybridization to fit this geometry (which is what Pauling actually figured out) w/ by the right no. of hybridized orbitals. It is true that the number of hybrid orbitals does equal the number of orbitals actually used (but I would say what it equals is the no of bonds that exist in conjunction with the geometry).
4. More complicated hybridization on p 106 of Chem for Utterly Confused

Now that we understand & can visualize hybridization better let us proceed to answer how double bond mean pi bonds.

P107 Chem Utterly Confused
Shows it all.

also Zumdahl makes a critical statement on p 410

He says that in a C=C the π bond is formed from the unhybridized p orbitals (plural).

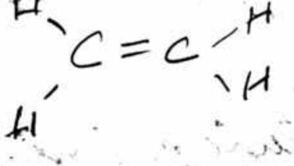
This is really interesting as unhybridized orbitals actually form the π bond.
There is more going on here than meets the eye. What you are noticing is that a hybridized orbital is a single lobe but that a unhybridized p orbital remains as a double lobe.
The double p lobe (unhybridized) is what form the double π bond,

The picture @ the bottom of p415 of Zumdahl shows this and how the electrons overlap and are shared between the unhybridized p orbitals.

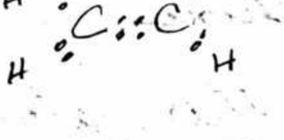
Finally an understanding of π bonds & their visualization

π bonds come from unhybridized p orbitals!

So now the question is, what becomes hybridized & what does not?
Lets look @ ethylene to get started.



Our sequence is
1. Lewis dot
2. VSEPR geometry
3. hybridization



Now for geometry

3 bonds, no lone pairs means trigonal planar
This means sp^2 and 3 lobes (also called orbitals but I like lobes more to keep them visually separated) that now give us trigonal planar.
But there is one p orbital that has not been hybridized.
This is what forms the π bond: A pi bond comes in pairs by definition, one above and one below. So when you say you have a double bond, now you can visualize it. One ~~comes~~ bond comes from overlapping sp^2 lobes, and 1 bond (even though) it exists as a pair, is a pi bond. This is great. I can visualize this now.

The case of sp hybridization and a triple bond is also interesting to look @. You have 2 π bonds with it.
~~So still~~ So you have 2 hybridized lobes of sp character, and two remaining unhybridized lobes that form 2 π bonds, for a total of 3 bonds

* Lesson: π bonds come from unhybridized p orbitals!!!

Now that we can understand & visualize hybridization, determine it, and visualize π bonds we can go back to our polar reaction in Murray India & follow along w/ his text description

I understand p118 now.
Double bonds (which ~~so~~ include pi bonds) are by their nature, ~~so~~ ~~nuclo~~ nucleophilic. As they have accessible electrons.

Double bond are therefore, by <u>their</u> nature reactive.

Continuing on p119:

Well, lets look @ what we did and see how it compare w/ his sequence.
Start again.

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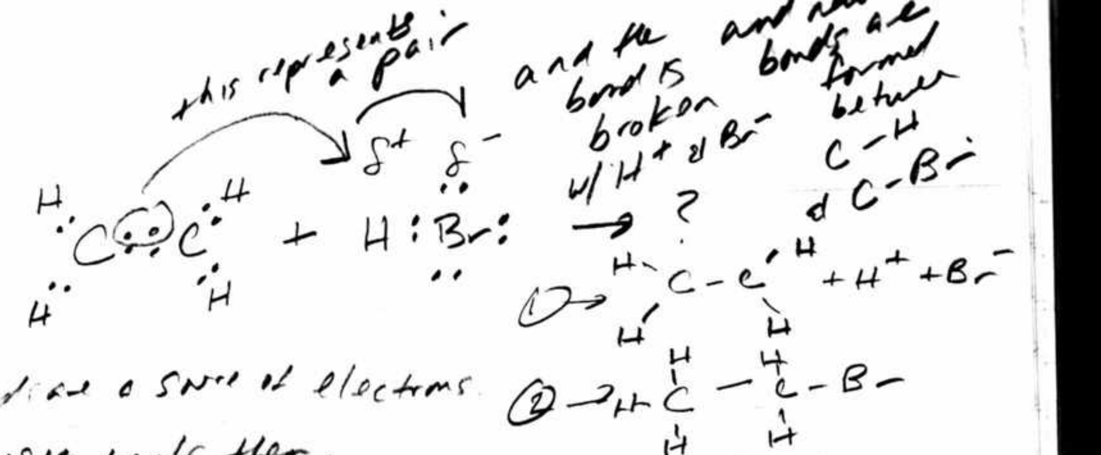
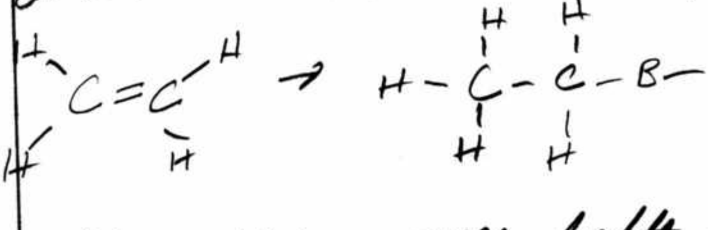


1. Double bonds are a source of electrons.
2. The hydrogen wants them.
3. The C=C therefore breaks and frees up two electrons
4. Where do they go? to the hydrogen.
5. This means the HBr bond is broken.
6. This means that we have H^+ and Br^-
7. This now moves an electron from H^+ to Br^-
8. And two new bonds are created, a CH & a CBr



This is good
It follows.

Ok, you are in much better shape now.
You might be able to start applying this
more towards your idea of

1. polymerization

2. free radical reaction (not very well yet)

3. A proposed reaction between Fe^{2+} & ~~COOH~~ aldehyde
Let's look @ this now.

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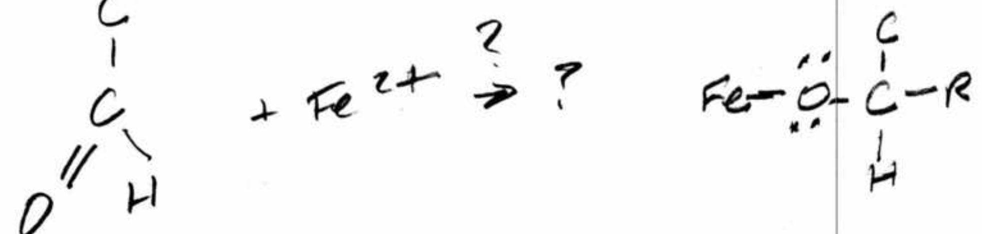
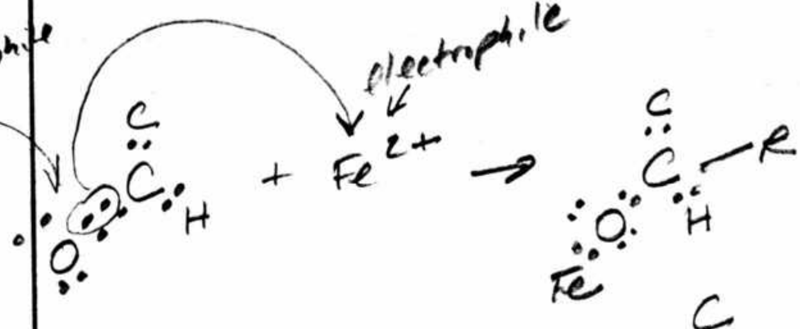
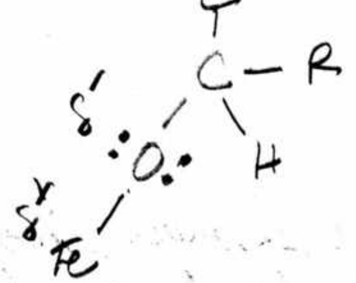
This is your idea





Another bond to C is required.



Start looking @ organometallics to see if these show up.

You have worked through p 122 Murray India. You need to get through 132 as there's much of importance here.

Roberts - Exp. Org. Chem p 545 has a chapter on organometallic chemistry!

Tomorrow we go back to the blood spectra [redacted] and continue.

The microbiology book by Brock I now have on pp 68-69 is giving critical information on lipid ~~structure~~ w.r.t. the domains of life.

Our hypothesis of cross domain remains correct.

Ester
Ethers } linkages

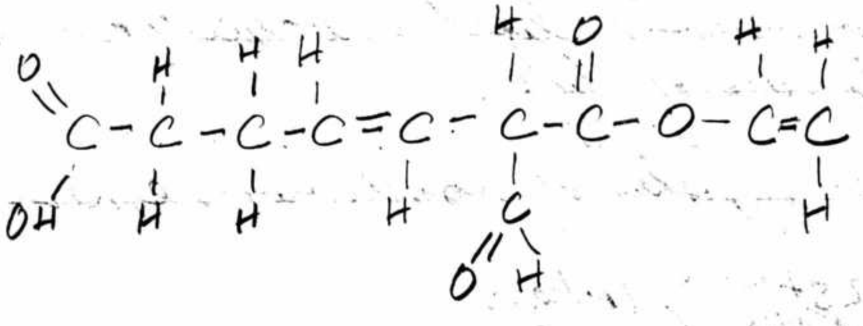
& terminal alkenes are telling a story of cross-domain construction

Within the lipid structure is the key to genetic origins.

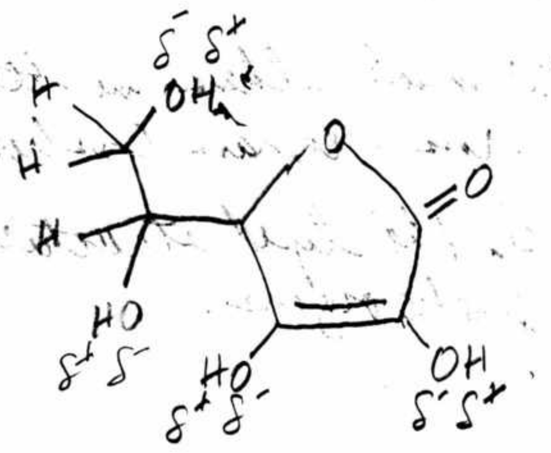
Page 134

Let's start to look @ the COB - Ascorbic Acid Interaction:

COB Proposed:



Ascorbic Acid:



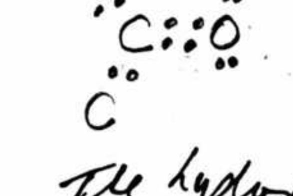
So what
could happen here?

1. The double carbon bonds w/in COB are reactive points since they are a source of electrons from both double bond & pi bonds.
I wonder which is more reactive C=C or C=O?
I suspect C=O because of electron source, pi bonds & polarization as well.
These are nucleophiles.
But try the central internal alkene bond first.

Proposed free radical consumption by ascorbic acid (multiply effect by 4 OH groups).

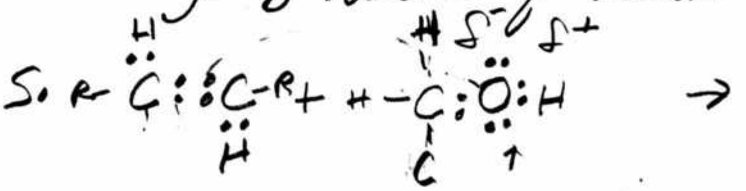
Now, w.r.t. ascorbic acid, are there electrophiles available?

The double bonded oxygen looks ~~[illegible]~~.

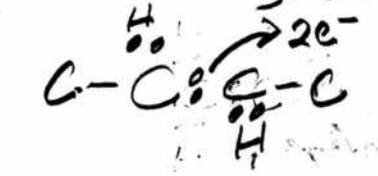


This would also seem to be a nucleophile so that is not helping very much.

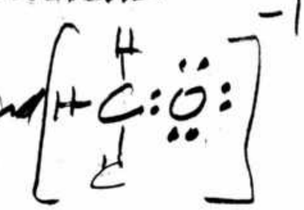
The hydrogen becomes of interest as $\overset{\delta^-}{O}\overset{\delta^+}{H}$

So 

1. So the C=C goes to C-C and frees 2 electrons



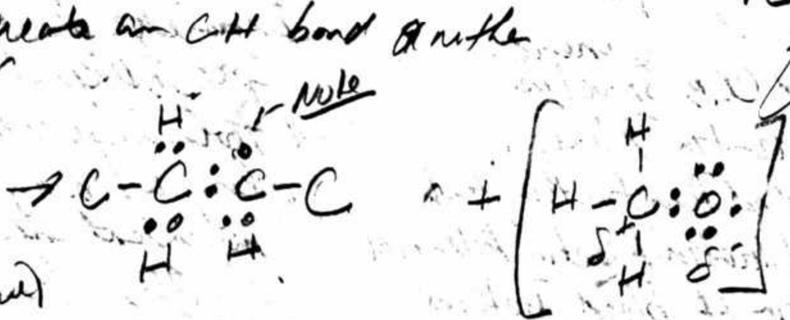
and we have H^+ and



So one electron can be used to create an C-H bond & another

FC of C = 4 - 4 = 0
O = 6 - 1 - 6 = -1

But O is more electronegative. Why would C be able to attract a lone electron? Wouldn't O form a bond with C? I think so.



(the H⁺ want [illegible]) along of electrons from the double bond

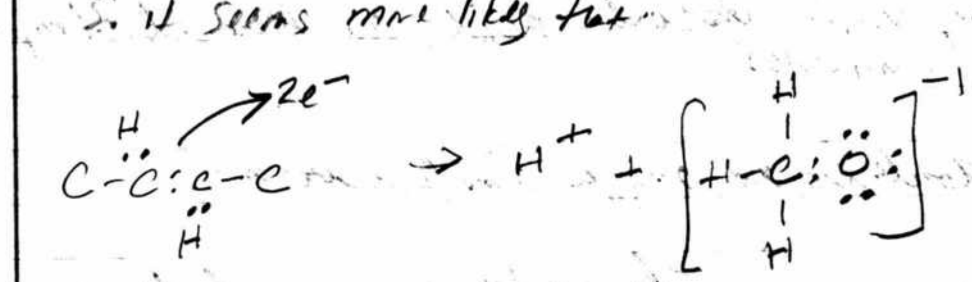
Both of these structures all now want to react with free radicals.

FC of C =
4 - 3 - 1 = 0

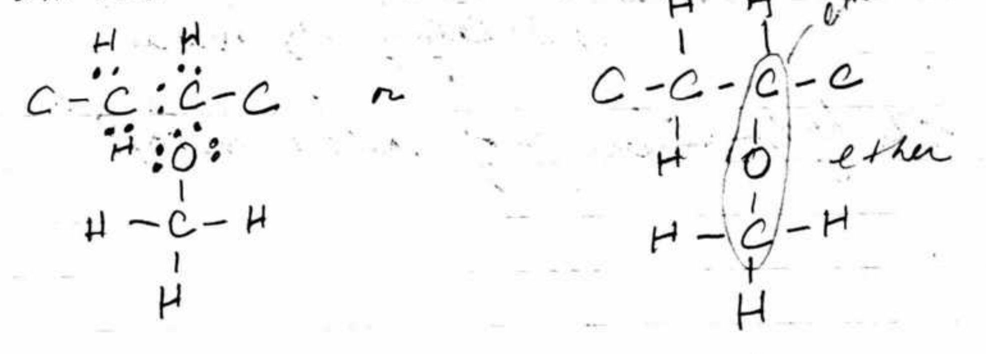
FC = 6 - 1 - 5 = 0

Discovery Topics on OR-CA Trip

So it seems more likely that



will lead to



So this shows how an alkene may be transformed into an ether?

Ok, back to [redacted] Blood interp.

Our Discovery Topics are:

1. Proposed CDB Generic Structure
2. Polymerization Potential
3. Free Radical Reaction Potential
4. Fe^{+2} Utilization Reaction Potential
5. Disruption of blood Proteins
6. Applications of Polymerization
7. Prospective Vit C Reaction Mechanics
8. Genetic Origin @ Domain Level - Prospective
9. We have substantially matched Polish Research Team Blood IR Profile - Janus
10. MRP is live
11. Free radicals, polymerization & alkenes are tied in w/ each other P186 Murray/India

In addition, my knowledge of IR Spec Interpretation & Tools Acquired, along w/ a major improvement in Org Chem knowledge including reaction mechanisms

(cont.)

12. radicals + alkenes = more radicals p184 Murray India
13. Tyndall Effect 15. Halogens react easily w/ alkenes
14. Molecular Weight Determination

May 11 2015 Monday

Returning to [redacted] Blood IR Interpretation:
We acknowledge the activity @
2390 - 2320 C≡N, C≡C, N-H $(NH_4)^+$
2190 - 2100 C-N, C≡C, C≡N
We do not record @ this time, but keep in back burner for further analyses
We go back to major activity between 1770 - 900
~~Sharp steep drop 1410 - Halos.~~
IR Spec 1780 - 1670 is Carbonyl
may also have ester or ketones (?)

The next most clear peak is @ 1492
We do not seem to have a great match here.
~~Benzene ring is weak (?) 1450 - 1600~~ IR Spec
ok, except our signal is strong ?
~~Alkane @ 1470 C-H is strong so that is OK.~~
~~Nitro N-O aromatic @ 1520~~
~~Nitro N-O aliphatic @ 1540.~~

TB:
~~1470 - 1450 Alkane CH_2~~

These are now entered.

The next thing we see in the last table is quite a bit of activity in the range of 1670 to 1060
~~these~~, from Stuart and Jane ~~[illegible]~~ most likely originate from amino acids.

Do not assume this yet. Use conventional approach

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1620 appears to be our first one.

IRSpec ~~1640-1560~~ Amine NH primary.
~~1680-1620 Alkene~~
~~1645 Alkene~~

TB ~~1680-1630 Alkene C=C~~
~~1680-1640 Amide C=O~~
~~1680-1620 Oxime C=N~~

Where do we stand now?

OH	94%
Amine	94%
Amide	94%
Alkane	95%
COOH	92%
Alkyne	81%
CO Carbonyl	91%
NO Nitro	90%
Benzene	59%

1250 now:
IR Spec 1300-1250 Carboxylic Acid
1260 Alkane
1260-1220 C-O Aromatic

What you are seeing is that you need the newer instrument.

Page 139

All of the work will be much improved with ~~the~~ new instrument ..

On the [redacted] blood, the activity is not pronounced enough to sort it out.

Conclusion: You need the better instrument now.

It almost seems as though the vertical range of the peak should be a weighting factor.

You could have a weighting factor from 1 to 0.

$\underline{\underline{dT}}$ $\underline{\underline{d\%T}}$

Weight factor = $(d\%T)^{.25}$

OK we have weighted this and it looks much better.

OH	90% ✓
Amine	81% ✓
Amide	86% ✓
Alkane	94% ✓
Alkyne	71% ✓
COOH	86% ✓
C=O	~~43%~~ 40%
N-O Nitro	64% ✓
Benzene	33%
Alkene	80% ✓

alkane	94%
OH	90%
Amine	81%
Amide	86%
COOH	86%
alkene	80%
alkyne	71%
N-O Nitro	64%
C=O	40%
Benzene	33%

This really does look better

We could propose a cut off @ 85%.

or 70% or whatever you want.

This is much better. You can now set the cut off @ whatever you want eg 70%, 85%, etc. 80%

There is a way of forcing you to not work w/ small isolated peaks.
I would suggest an 80% level @ this time.

Now we have one more large move.
750 to 600 or less.

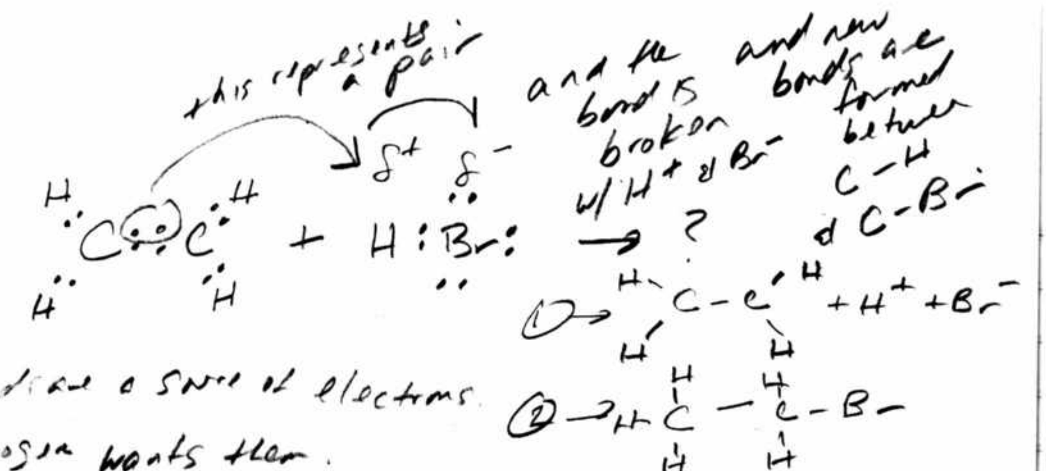
IR Explain
~~Alkyl Halide 800-600~~
~~Alkynes ~700-600~~

TB ~~Alcohol 770-620~~
~~Halide 700-550~~
~~Alkyne 700-600~~

~~IRSpec Alkyl Halide 800-500~~

So alkyne is still in the picture

Use Cutoff of 1500 for Fingerprint Region



1. Doublebonds are a source of electrons.
2. The hydrogen wants them.
3. The C=C therefore breaks and frees up two electrons
4. Where do they go? to the hydrogen.
5. This means the HBr bond is broken.
6. This means that we have H^+ and Br^-
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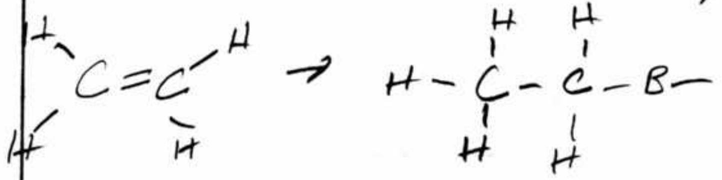
8. And two new bonds are created, a CH & a CBr



This is good.
It follows.

Ok, you are in much better shape now. You might be able to start applying this more towards your idea of

1. polymerization
2. free radical reaction (not very well yet)
3. a proposed reaction between Fe^{2+} & ~~COOH~~ aldehyde
   Let's look @ this now.

You have done excellent work here
Suggest a ~~70%~~ cutoff level @ 80% for now.
You match Janus surprisingly well.

Now our set is:

		Ranked	
OH - Alcohol	86% ✓	Amine NH	87%
Amine - NH	87% ✓	OH Alcohol	86%
Amide	86% ✓	Amide	86%
Alkane	81% ✓	COOH	86%
Alkyne	71% ✓	Alkane	81%
COOH	86% ✓	Alkene	80%
C=O Carbonyl	40%	Alkyne	71%
N-O Nitro	43%	Carbonyl C=O	40%
Benzene	23%	Nitro N-O	43%
Alkene	80% ✓	Alkyl Halide	36%
Alkyl Halide	36%	Benzene	23%

I would recommend that we work @ the 80% level as a first guide.

You ~~could have cutoff~~ @ the 70% Level

Now Compare w/ Janus.

Janus has NH
OH
CH
CH_3
CH_2
C=O

Notice that he also has PO^{2-} and I saw this and skipped it.
~~1320~~ 1040-910?

May 14 2015 - [redacted]

Let's get organized. Limited time available:

[redacted]

2. Preparing for Instrumentation to come on board. You know that you simply do need the newer instruments

3. Continued examination of reaction mechanisms. Problems are the best approach here.

4. Stuarts Book on IR interests me a great deal on Biological Aspects.

5. Ch 5 Murray India is a gold ~~[illegible]~~ mine. You are @ sec 5.7 but 5.1 - 5.6 need much study -

I think you really do need to work through Chap 5.

Murray Ch 5 India Problems are important to understand.

I missed so many of these of Prob 5.1 that I need to go back to the drawing board.

a) $CH_3Br + KOH \rightarrow CH_3OH + KBr$

Now, my verbage was:

JOIN ⟷ Addition
SPLIT ⟷ Elimination
SWAP ⟷ Substitution
REARRANGE ⟷ Rearrangement

Now, my answer for the above was rearrange. But this is clearly wrong. This is definitely a swap. Swap means substitution and this is the correct answer. So I really had no idea what I was thinking on this one.

b) Now lets go to #2.

$CH_3CH_2Br \rightarrow H_2C=CH_2 + HBr$

NO! NO! NO!

What do you see here? (I said swap)
No, it is not swap. I see ~~[illegible]~~ some splitting taking place here. Splitting is elimination. The answer is indeed elimination. You simply did not study this properly!

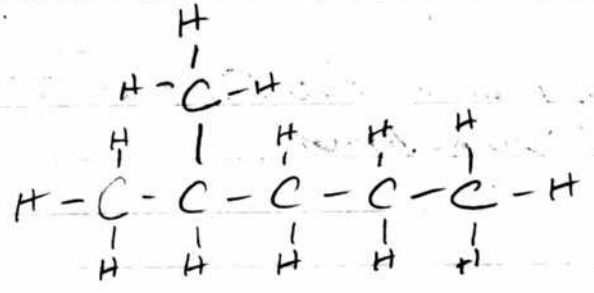
c) The last one:

$H_2C=CH_2 + H_2 \rightarrow CH_3CH_3$

This is clearly joining. Join means addition. Again, I did not even look @ the problem properly.

Page 144

2 methyl pentane
C_6H_{14}



$C_6H_{13}Cl$

$\cdot\ddot{\underset{\cdot\cdot}{Cl}}:$

This is a real problem & great to work with. What do we know?
Chlorine is very reactive.
It is also very electronegative.
So where is it more likely to react & why?
Why is one hydrogen different than another?
Why couldn't it react anywhere w/ H?

First of all, we are using Cl_2, not Cl so

$:\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}:$

Now, this definitely has an excess of electrons available.
So this is a nucleophile.

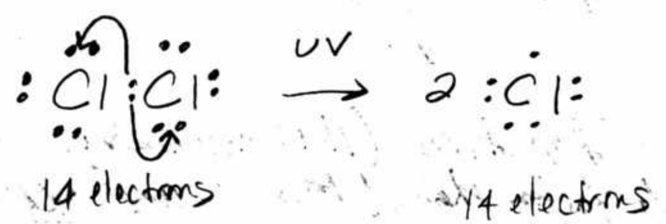
Reading the text, we see that Cl-Cl is a relatively weak bond. How weak I wonder? ΔH = 58 for Cl-Cl
ΔH for C-C is 83 units
C-O is 85

There is also a bond energy table on p 125 Murray India.
H-H 436 kJ/mol
C-C } Sorry Charlie
C-O } not available in this table.

Page 145

OK, back to the problem... Well, back to the text on p113 about radical reactions.

We start by noticing that UV is sufficient to ~~[illegible]~~ break Cl_2 bonds.
So Cl_2 + UV light $\rightarrow 2\ \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$
notice what he does:



So this results in a lone electron, or radical, on each separated Chlorine

Now it seems to me that the electrons did not actually move. What the arrow is showing is what ATOM the electron goes to, not specifically where the electron goes to "within the dots".

What we see next is that a Cl radical "collides" with a methane molecule. We notice that we have 3 such places on our starting molecule.
So he is saying collision is sufficient along w/ weaker bond of Cl – Cl. But it seems to me that ΔEN should also be a factor. ΔEN = 3.16 – 2.2 = 1.0 clearly polar covalent.

~~Next we have two methods that can occur.~~
(Cont)

What looks to be the heart
of understanding Organic Chemistry.

May 15 2015

I have now reviewed the radical reaction section to develop a broader understanding.

We do see now the wonderful elegance and at one level simple elements that define organic Chemistry. It seems that we have only two primary methods of reaction that take place.

1. Polar Reactions (It is asymmetric electron movement)
   The factors that determine and affect polar reactions seem to be primarily
   1. Electronegativity
   2. Size of the atom
   3. Distribution of electrons in the valence shells.

where.

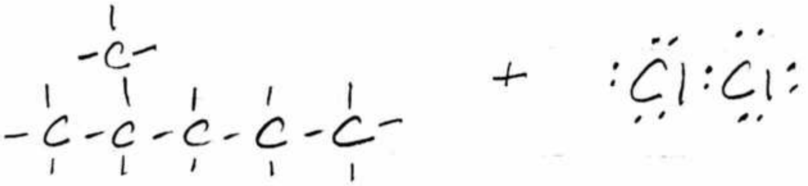
p116
Murray
India

2. Radical reactions (symmetric electron movement
   We see that radical reactions ultimately involve the symmetric movement of electrons within a bond, either single or a double bond (a double bond goes to a single bond)

It is frequently a chain reaction.
It ~~always~~ usually has 3 steps:
1. Initiation (formation of a radical to begin with)
2. Propagation - the chain reaction
3. Termination - it eventually stops somehow.

So now I have a conceptual framework and this is great.

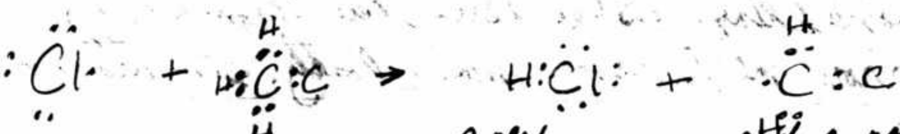
But unfortunately, I am not sure if I can really understand or solve Prob 5.2 p133 Murray 2nd Ed yet. So lets go back.



2 methyl pentane C_6H_{14}

Initiation

1. What do we know?
   Cl double bonds are weak and can be broken to create 2 Chlorine radicals. $Cl_2 \rightarrow Cl\cdot$ and $\cdot Cl$ (radicals)
2. H can react w/ these s.



a new compound

and a new free radical and also a modified compound.

Propagation

This becomes immediately obvious when you really draw Lewis. you do like Lewis it helps you (become necessary) to visualize.

3. Now this new radical reacts even further w/ the original Cl_2 to create another free radical.

Now at some point it all has to end. Lets see what we have available to us with Chain reaction process:

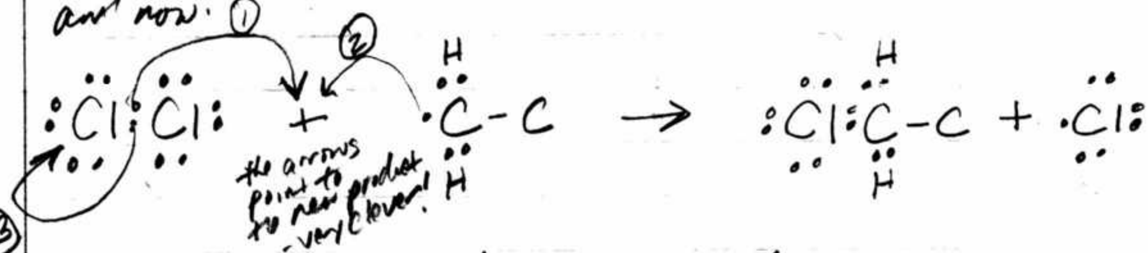
$$Cl_2 \xrightarrow{UV} Cl + Cl$$

with UV light

$$:\!\dot{Cl}\cdot + H{:}\overset{H}{\underset{H}{C}}-C \rightarrow H{:}Cl{:} + \cdot\overset{H}{\underset{H}{C}}-C$$

and now.

without UV light



$$:\!Cl{:}Cl\!: + \cdot\overset{H}{\underset{H}{C}}-C \rightarrow :\!Cl{:}\overset{H}{\underset{H}{C}}-C + \cdot Cl\!:$$

Even though we identified that electrons attach to an atom, it does seem as though they do go to a bond, but ultimately the bond belongs to an atom so let's go with that.

OK, some things that we learn here from studying the arrow mechanisms more closely. It was not intuitive.

1. The arrows point to an atom, not a bond
2. The arrows point to the plus sign as a product! ①
   This is very clever and avoids drawing arrows across the reaction. It is a good logistical solution to a problem.
3. As a free radical reaction, we must see that the arrows must come from two symmetric sources ①&② (i.e. in this case, reactants). You CANNOT take them from a single source.

4. Understanding this allows you to see now how the new radical is formed. ~~It does not, AND THIS IS NOT INTUITIVE,~~ ~~a~~ If you actually see what the arrow is doing it is doubling back on itself, or staying retained within the original Cl_2 bond. The arrows are great, but you do need to think them through and follow the rules. ②a③

Understanding here is slow, but it sure is worth it and powerful when you have it.

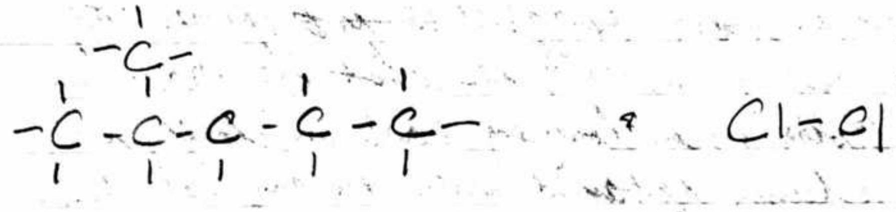
What we see next is that this reaction will go on forever as long as you have a supply of Cl_2 + CH_3.

There is another way that it can be stopped. By two free radicals joining together. They can be many combinations, they do not have to be of the same molecular form.

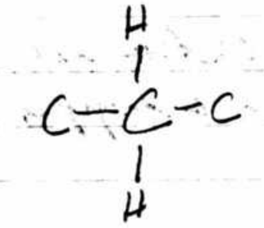
This is fairly infrequent however. Collision reactions of this type are fairly rare.

Now we understand more clearly how Murray's textbook example has proceeded and we learned quite a few things in the process.

Now we go back to the original problem again.



Our free radical solution certainly appear to apply equally to methane & methyl groups (CH_4, CH_3). Does it apply also to methylene groups?
So what happens with:

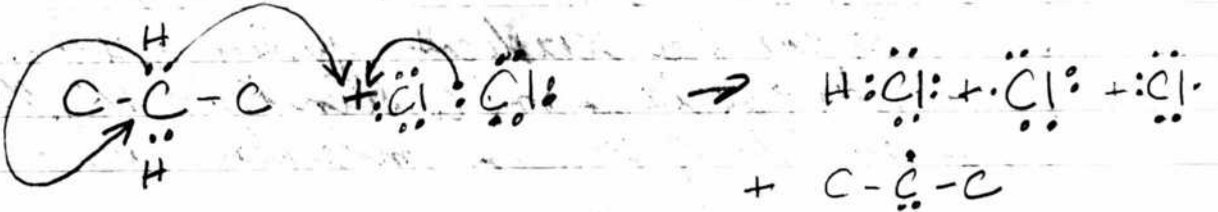


?

It was UV light that caused this to happen not hydrogen.

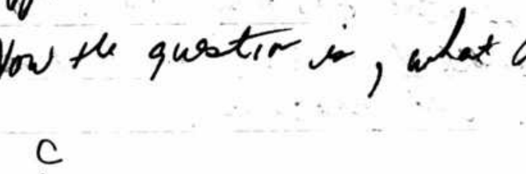
and Cl-Cl
which goes to $\cdot\ddot{\underset{\cdot\cdot}{Cl}}:$

1st Stage only, there are two stages



Seems to me it could still happen fine the same way @ any H site, but key on the ends may be different than in the middle of the chain.

Now the question is, what does the second stage produce?



This does not appear to work

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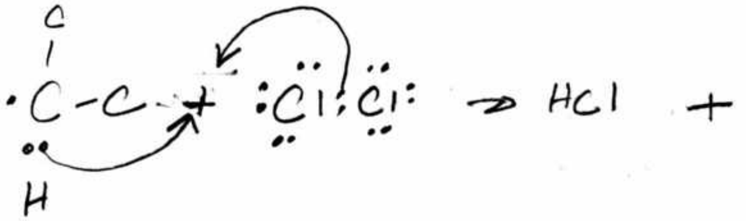
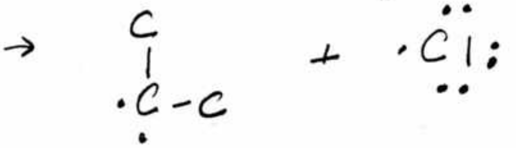
So what would happen in a reaction here?
Try it

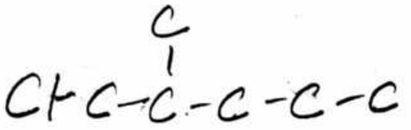


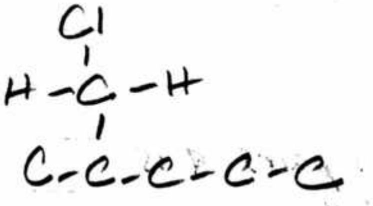


But there are no hydrogens left to bond to ~~the~~ Carbon
The reaction does not seem ~~[illegible]~~ feasible.

My take is that the radical reaction takes place w/ methane & methyl groups, not methylene.

This now says we should have 3 places where Cl attaches





This is my proposed answer.

There are 5 answers.
1, 2, 3, 2, 1

I missed something here. It is every carbon on the main chain that allow for this reaction to occur.

1 Chloro 2 methylpentane
2 2
3 2
2 4
1 4

Some Comments on Oxygen therapy

Oxygen Therapy? [illegible]

1. Fe^{++} + H_2O_2 → free radicals

2. Culture growth explodes in the presence of Fe^{++} + free radicals
Conclusion: Cancer growth explodes in the presence of free radicals

3. Ozone as [illegible]
Is Smog [illegible]
Does smog kill plants?
What is the chemical structure of smog?
C=O (carbonyl groups)

4. [illegible] amino acids

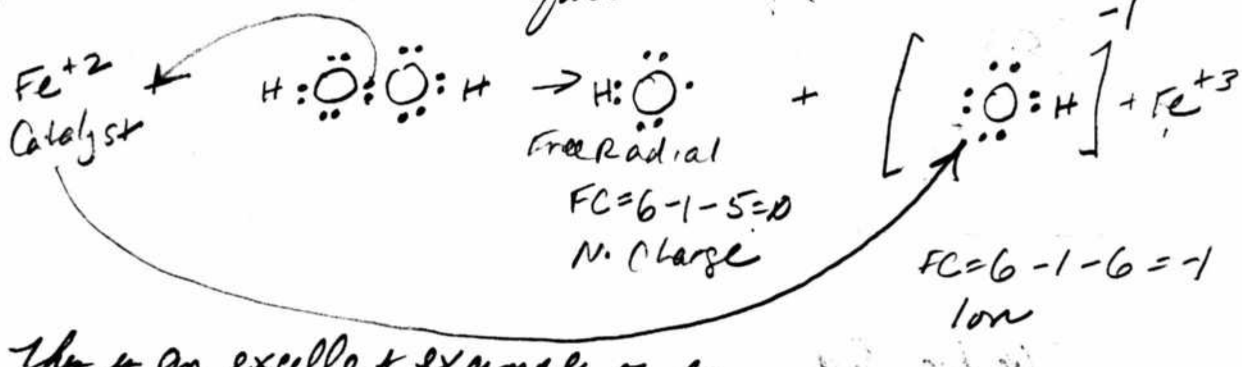
[illegible] carbonyl [illegible]
Also Murray has demonstrated [illegible]
upon carbonyl amino acids

~~4. [illegible]~~

5. Remember that O_2 itself has lone pairs & is therefore a "free radical"

Fenton's reaction examined again

Fentons reaction examined further:



This is an excellent example of a free radical productions
The splitting form

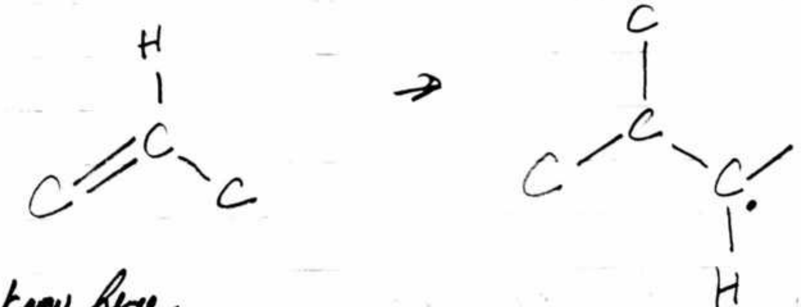
Free radicals can form by:
1. Splitting a bond (not always symmetrically)
2. Taking electrons from a double bond and reallocating them (also always symmetrically)

1. Polar reaction are asymmetric wrt to electron movement
2. Radical reactions are symmetric w.r.t. electron movement.

Alkene double bonds are prone to free radical formation & ~~polymerization~~ Terminal alkenes are prone to polymerization
Carbonyl groups are prone to reactions w/ ~~amenes~~ amides ~~to form~~ and to form alcohols & carboxylic acids.

Many Ch 5 problems are very intriguing

5.3



We know here
that a double bond has been broken.
and a lone pair electron, ie free radical has been created.
Is this a polar reaction (asymmetric - ie both electrons go to one product)
or
free radical reaction (symmetric) an electron goes to each product.

To me, it is a ~~free~~ radical reaction.
One electron becomes a lone electron
and the other forms a hydrogen bond on a separate carbon. Also, in the process, a double bond (the source of the electrons) is reduced to a single bond.

I have this one right.

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5.A Nucleophiles & electrophiles

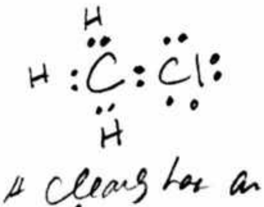
Nucleophiles have an excess of electrons so they can be negatively charged

Electrophiles have a deficiency of electrons so they can be positively charged.

5. b) is negatively charged. It is therefore a nucleophile.

Now for others.

a) CH_3Cl Carbon is electrophilic



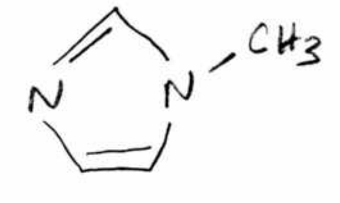
$\Delta EN_{Cl-C} = 3.16 - 2.55 = 0.71$

moderately polar bond.

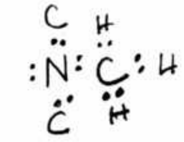
Cl clearly has an excess of electrons.

this says to me it is a nucleophile.

c)



Also the double bonds are a rich source of electrons & pi bonds.



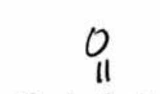
$\Delta EN_{NC} = 3.0 - 2.6$

$= 0.4$

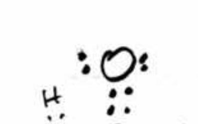
not polar

I say nucleophile because of the nitrogen lone pair

d)



$CH_3\overset{O}{\overset{\|}{C}}H$

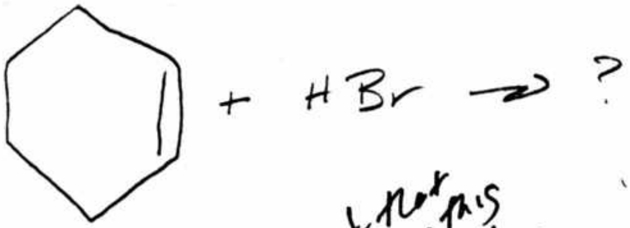


to me it is also a nucleophile.

May 19 2015 Tues

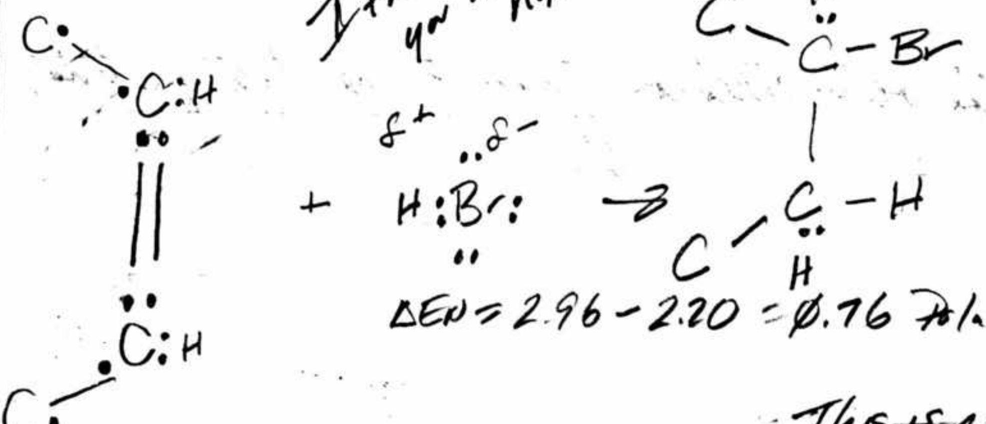
There are a lot of interruptions taking place in conjunction w/ social calls & presentations. This has been taking place for the last week now. But there has also been some good progress. I have prepped fairly well for the instrument arrival.

Prob 5.6 Murry [illegible]



principle: double bond want to go to single bond in the presence of a partially polarized hydrogen.

I think that you have this right.



This is what I see.

ΔEN = 2.96 − 2.20 = 0.76 Polar Covalent

This is a "join" reaction i.e., an addition reaction.

The double bond is a source of electrons. This makes it a nucleophile. Hydrogen is an electrophile.
~~There is no reason for~~

HCl causes the same reaction to take place w/ HCl..

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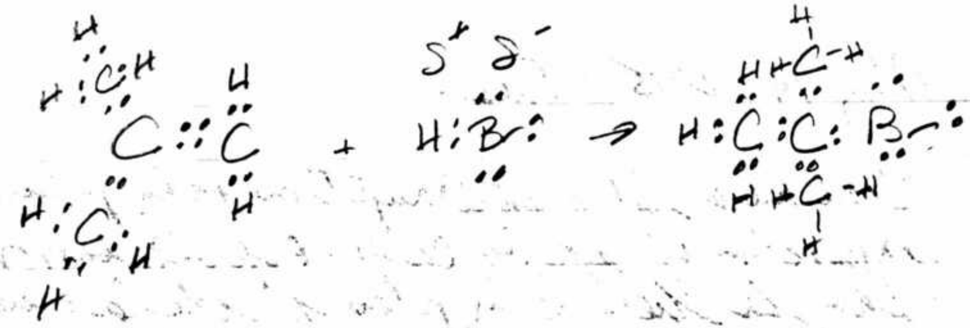
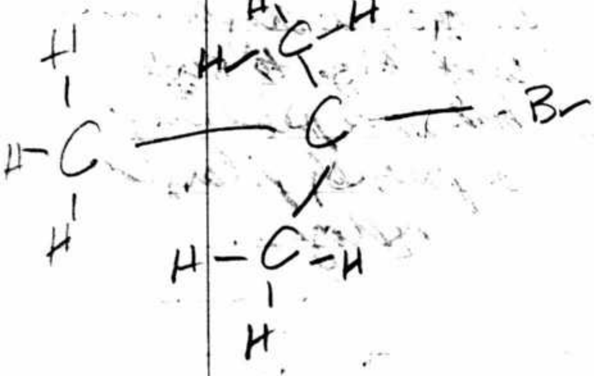
5.1



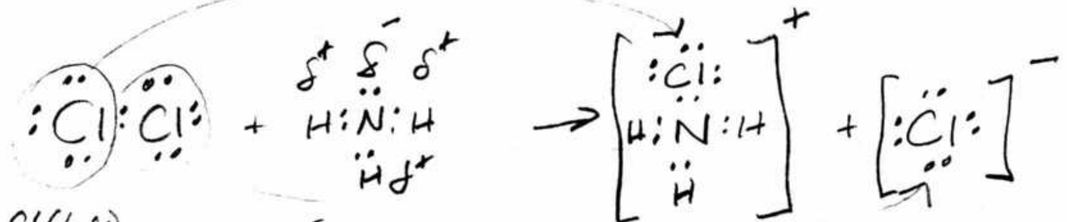
1. Double bond goes to a single bond.
2. This frees 2 electrons.
3. One electron forms a bond w/ Bromine



4. The other electron forms a new hydrogen bond.

Symmetric breaks are radical reactions
Asymmetric bonds are a polar reaction.

5.0a He would like me to add arrows!



FC Cl(left) = 7-1-6=0   FC 5-3-2=0   5-4=+1   7-0=-1

So, what has happened in this reaction?
Cl is highly electronegative. But so is N. ΔEN = 3.16 - 3.04 = .12
So electronegativity is not a huge factor here.
But for Nitrogen & NH ΔEN = 3.04 - 2.20 = .84
So this counts. So we have ~~H~~ $^{\delta+}NH_3^{\delta+}$
Therefore we have a partially polarized hydrogen.
In addition in NH_3 we have a nucleophile.
But why in this case does the Cl_2 bond break?
This is a polar reaction. So what is causing the polarity?
The only thing we have is a slight increase in Cl over N.
This is a curious affair

I do not really see it in terms of electron flow
so much as I do in terms of splitting of a bond.
But if a bond splits then there is electron movement
and here it is asymmetric & a polar reaction.
That is what I do know.

Double arrow means pair
of electrons

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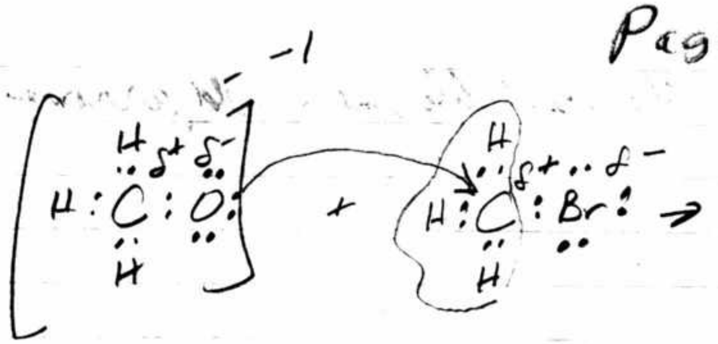
5.8.



FC = 4-4 = 0

FC = 6-1-6 = -1
O normally has two bonds

·Ö·

So our species has an
extra electron & is
C-O is polarized
Br-C is polarized
Now H_3CO is an nucleophile (excess of electrons)
* The C:Br bond breaks - why?

But, once it does break, the O wants to bond
with the C, which it does and Br is left
alone as an ion. This is a polar reaction

243 We know now why Cl-Cl bonds break. p125 Murray India
~~263~~295 Now we also know why $(CH_3)_3C$-Br breaks.
C-Br is 276
These are relatively weak bonds so that is why it
happens. This is a really important explanation
It tells you if something is likely to happen or not.

FC = 7 - 8 = -1

FC = 6 - 2 - 4 = 0

Tables of Bond Energies are

1. Murray - India p 125 generally organic

2. Zumdahl - p 372 More general
Halogens and multiple bonds are also there.

These tables are actually very instructive. They set the stage for nucleophile & electrophile reactions.

So now you know how to set the stage.
Notice CH & OH & CO are very strong.
The halogens are especially weak.

On to Prob 5-8c

Some Comments on oxygen therapy

"Oxygen Therapy"

1. Fe^{+2} + H_2O_2 → free radicals

2. Culture growth explodes in the presence of Fe^{+2} + free radicals.
Conclusion: Culture growth explodes in the presence of free radicals

3. Ozone is smog.
Is Smog good for you?
Does smog kill plants?
What is the chemical structure of smog?
C=O Carbonyl groups

4. NC Study of effect of ozone and amino acids.
ie formation of carboxylic acids COOH
also Murray has dominating emphasis upon carbonyl amine reactions

~~4. Acids react w/ alkenes (C=C) to form~~

5. Remember that O_2 itself has lone pairs & is therefore a "free radical"

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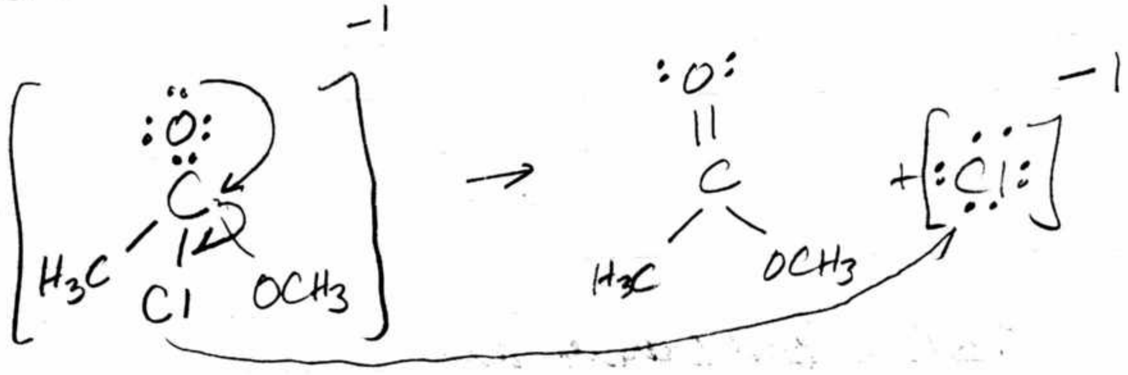
5.8c



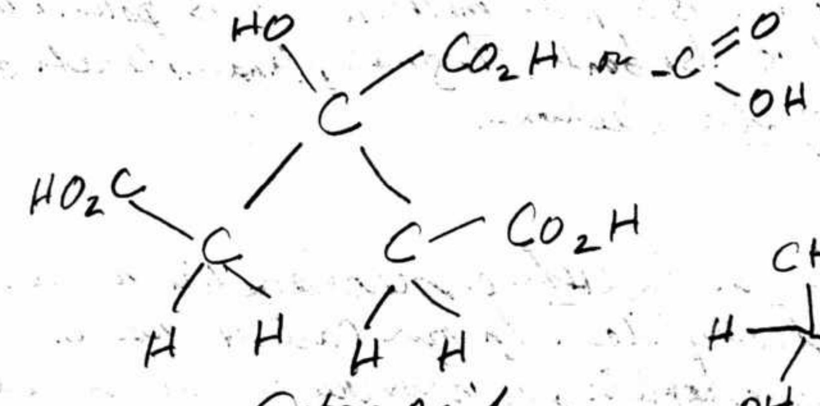
(C) FC = 4 - 4 - 0 = 0
(O) FC = 6 - 1 - 6 = -1
This is a [illegible]
nucleophille?
It wants to give away
electron.

I am sure we have some things to look @ here.
The oxygen here is a nucleophile. So it wants to
get rid of some electrons.
So where do they go? 1st the double bond C=O.
but if they do this, the FC of the C becomes

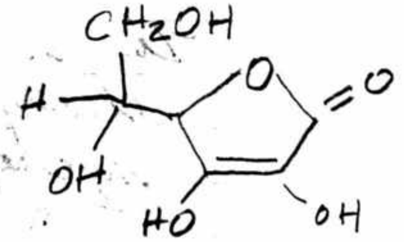
$\dot{C}=C$ FC : 4 - 5 = -1 So now the C
becomes a nucleophile, So it wants to
get rid of an electron as well as break
a bond. So it pushes it on to the
Cl and it breaks the bond and makes
it a Cl ion.

I can describe it in words what happen and I can see what it does but I cannot draw the arrows very well.

5.9 Citric Acid is: $CO_2H = COOH$
(P54 Murray Indian)



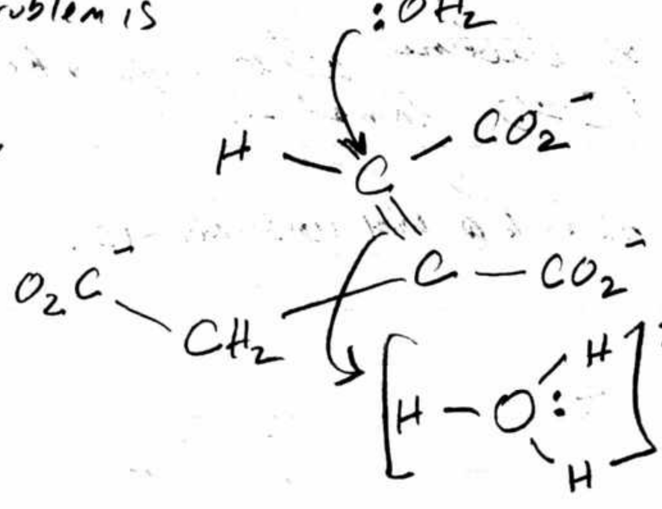
Citric Acid



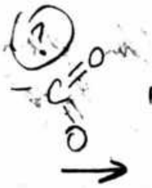
Vitamin C

Our problem is

Citric Acid Intermediate



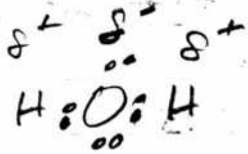
$FC = 6 - 3 - 2 = +1$



$FC = 4 - 5 = -1$
?

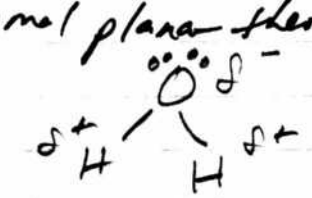
This will require some examination.
For the immediate interest, I would like to know how Vit C corresponds w/ Citric Acid.

Lets look @ $:\ddot{O}H_2$ first.



FC = 6-2-4=0 O1a

So this is a water molecule. It is polarized. It is also bent. Trigonal planar theoretical because of free electrons.

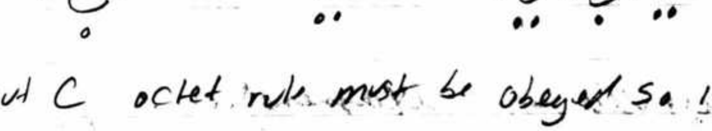


This can be either a nucleophile or a electrophile. In our case it is a nucleophile by providing a pair of electrons to a C=O bond.

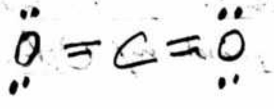
The pair of electrons allow for the double bond C=O formation?

Lets look back @ what Carbocation is.

What is the structure of CO_2? Octet rule must be satisfied

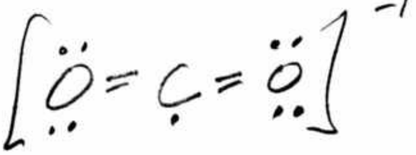


but C octet rule must be obeyed so it is



This is CO_2 FC= 4-4=0

Now CO_2^- must have an extra electron so



FC= 4-4-1 = -1

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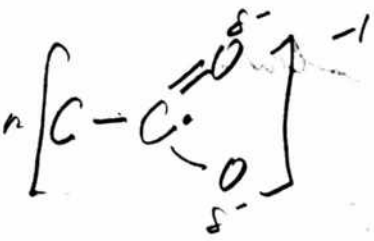
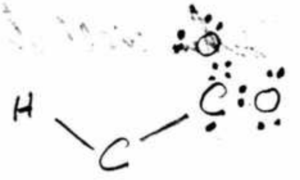
The $H^{\delta+}$ was pulled off and apparently the electron less moved to to C?

FC= 4-4-1 = -1





FC= 4-4-1 = -1

For this case, CO_2^- is not self standing. It is bound to another C. So this does change things. It does indicate one double bond & one single bond like we are showing

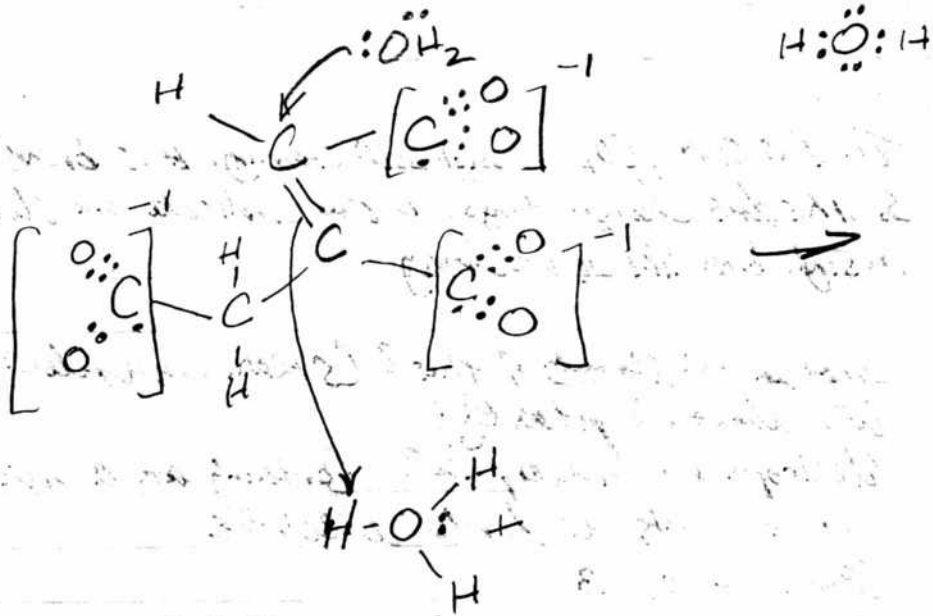
What is the geometry of this? (stearic number?)
What about the polarity?
Electrophile or nucleophile? Certainly as a nucleophile.
So it wants to donate electrons
Stearic n = 3
FC = Valence - sticks - dots
Stearic = No. of bond groups + no. of paired electrons :
MULTIPLE BONDS COUNT AS SINGLE !!!
A stearic number is only the geometry (arrangement) of the electron pairs (bonded or free count equally). The structure (actual) and the name, however, are based upon the actual atoms involved.

So back to our ~~structure~~. Ours is indeed trigonal planar.
(3 bonds, no free electron pairs)

So we have a trigonal planar nucleophile. It should also be polar w/ a dipole moment.

Summary: It wants to get rid of an electron. ~~or gain a proton~~. (octet rule).

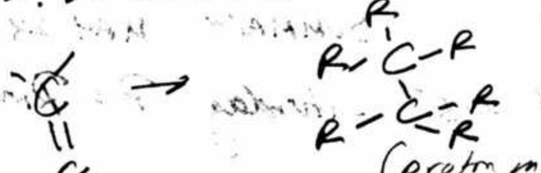
so lets move on, she will be slow.



We know now that the CO_2^- groups are nucleophiles. We know that water is added to the compound. Water can be either a nucleophile or an electrophile, in this case it is ~~shown~~ presented as a nucleophile.

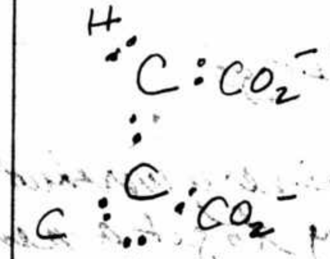
It shows two free electrons shifting to the C atom. This now turns the C into an ~~electrophile.~~ nucleophile (excess of electrons. and it may be what makes the doubled bond. Either way, the double bond needs to break and the electrons from it have to move asymmetrically toward another water molecule.

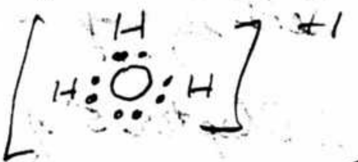
Part of the answer here was realizing that C wants to make four bonds. So we should have seen



This alone would have gotten us a lot closer.

(proton migration)





$FC = 6 - 3 - 2 = \boxed{+1}$

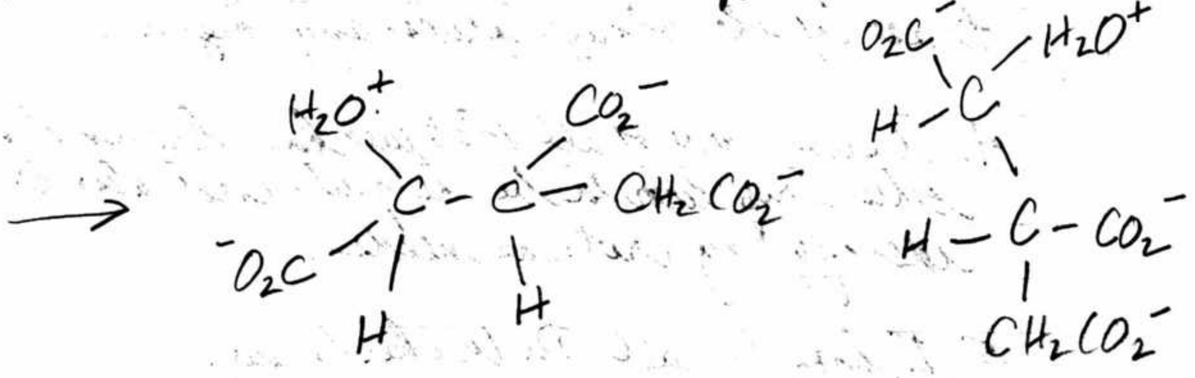
① We know that the water molecule inherits a proton which makes it H_3O^+

② We know that CO_2^- groups wish to inherit a proton.

③ We anticipate that the double bond become a single bond.

after that we get pretty much stuck other than anticipating a single bond Carbon.

We have that part right, which is good. Structure generated goes to.



Now we are going to start working on energy changes.

SUMMARY MAY 23 2015

May 23 2015 Saturday Pit River NE Calif

Let's regroup on where we would like to go:

1. Chapter 5 of Murray - India is very worthwhile and deserving. You are starting to get a sense on organic reactions now. They certainly are interesting and a phased in study approach would be very helpful. The workbook may be your best source for this.

2. In Murray, we are starting to look @ energy transfers. This is also extremely important and helpful since it will help you to understand if a reaction is likely to take place or not, or what it would take to make it happen.

3. The microbial fuel cell experiment yesterday was certainly interesting and it opens up another entirely new line of research. You could repeat this adding more dye (mediator) to see if the voltage peaks any higher.

4. A summary of all that we have learned on this trip would be helpful and also to identify any critical needs.

[redacted]

Iron and siderophores & Lyme (not!)
p103 Madigan

SUMMARY MAY 23 2015

[redacted]

7. Play & lab time is also important.
You have the Biology kit with you.
You also have radio but it just does not seem very likely on this trip.

8. Mathematics is also very interesting. You need to become more familiar w/ the Casio. It is powerful.

[redacted]

10. Look @ yeast under the microscope?
Or is it in the textbook?

11. Today I learn that p964 Madigan Microbiology

Citric Acid $\rightleftarrows$ [Citrate + Fe^{+3}] complex!

This is undoubtedly very important.

It appears that the citric acid cycle is going to be very important to learn about.
Sec 5.13 Madigan p127

Iron in microbial nutrition is described on p103 Madigan along w/ the role of siderophores. *

*

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SUMMARY MAY 23 2015

Discovery Topics in the CA-OR Trip

1. Proposed Generic COB Structure
2. Polymerization potential (alkenes & COOH) EZ
3. Free Radical Reaction potential (alkenes - Murray)
4. Fe^{+2} Utilization Reaction Potential w/ COB Structure (Mg, Ca alternative)
5. Disruption of blood proteins
6. Applications of polymerization
    - a) stabilize blood @ high temperature
    - b) allow for biological activity of hemoglobin within solvents
    - c) drug delivery
    - d) tissue engineering

    "Conjugated Poly Acrylic Acid"
7. Prospective Vit C & Citric Acid Reaction mechanics
8. Genetic origin @ domain level w/ lipid analyses
9. We have substantially matched Polish research team (Janus) Blood IR Profile
10. MRP is live
11. Free radicals, alkenes & polymerization relationships
    Murray - India p 186
12. Radicals + alkenes = more radicals p184
    Murray India
13. Tyndall effect
14. Molecular weight determination, boiling pt, thin tube — p181 Barrons EZ Chem
15. Halogens react easily w/ alkenes
16. Citric Acid → Citrate - Fe^{+3} iron chelation
    p 964 Madigan Microbiology
17. Siderophores, Iron, & microbial metabolism
    Madigan p 103
18. Fuel cell prospects - lab experiment conducted
19. Qualitative Organic Chemistry Identification !
    Roberts - Chap 24 !

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SUMMARY MAY 23 2015

(Continued @ end of book.)

20. 19. IR & GC instruments are under contract.
Continue payment process.

21. A study of oxidation reduction reactions, relationship to nucleophiles & electrophiles, partial transfer & complete transfers of electrons and the "rules" of oxidation states

Some topics of study on the trip:

22. Bond Energy Calculation (ΔH) & exo-endothermic relationship as well as Keq!

Energy analysis →
1. Lewis structure   4. Polarity
2. Formal Charge   5. Electronegativity
3. Molecular Geometry   6. Acid base Chemistry
6. Electrophile - nucleophile relationships
7. Beginning understanding of aqueous chemistry reactions
8. IR spectra interpretation, multiple source analyses, probabilistic model development
9. Molecular structure development, Avogadro construction, ACD search & properties prediction
10. Covalent & polar covalent bond evaluation
11. Conductivity expected, solubility, MP & boiling point
12. Hybridization, σ & π bond understanding
13. Free radicals, lone pairs, Lewis structures.
14. Bond dissociation energies
15. Acids, bases, Conjugated acids & bases
16. Electron transfer & bond breakage & formation
17. The major divisions between polar reactions & free radical reactions, the asymmetry of polar reactions and the symmetry of radical reactions. p112 Murray Indian
18. Type of reaction in general

JOIN (addition)   SPLIT (elimination)   SWAP (substitution)   REARRANGE (rearrange)

19. Fenton's reaction understanding
20. Redox reactions

This Page Available

you see the special importance of:

1. Protein loss & disruption
2. Antioxidants, eg Vit C
3. Iron chelation & the citrate ion relationship
4. The acid problem, eg glutamic acid anxiety relationship
   valerian, taurine, theanine.

[redacted]

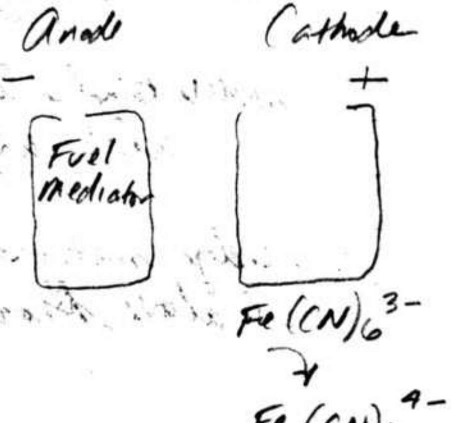
Thru Page Available

I mmediate prospects on tap are:

1. Meiosis - Mitosis lab - 1st part only
~~2. Lemon juice - tomorrow is better.~~
3. ~~Construct fuel cell model~~ w/ ~~3 stand methylene blue.~~ DID IT!
4. Continue w/ Murray Ch 5
5. Look for progressive practice organic reaction problems.

I have to say, the fuel cell construction is an excellent example of the need and benefits of understanding organic chemistry. There is a lot that is happening here

Fuel cell is composed of:
Electrodes
Catalyst
electrolyte
membrane



SUMMARY MAY 23 2015

and The Seven Steps Plan

1. Get the best IR spectrum and data that you can. Use pure compounds in the analyses.

2. Exhibit a high level of skill in IR spectra analyses

3. Develop a structural model & exploit the w/ search tools.

4. Compare the model w/ reference spectra & identify similar compounds.

5. Identify the most probable chemical reactions that are likely to take place

6. Understand these reactions
   what, why & how

7. Develop mitigation strategies based upon the above knowledge.

Looks to me like you need to study oxidation reduction reactions again.

When an element combines with oxygen, it is said to be "oxidized"
But oxygen does not always have to be involved in an oxidation reaction. Oxidation and reduction have been defined in more general terms.
But oxygen is commonly involved, such as

$$\overset{2(+2)}{N_{2(g)}} + \overset{2(-2)}{O_{2(g)}} \rightarrow 2NO_{(g)}$$

incidentally, N commonly has an oxidation state of +3
but it can also be +2, +3, +4, +5
Oxygen seems to be always -2

An ionic compound is made up of ions that combine together.
Seems to me the easiest thing to keep straight is that

~~oxidizers are electrophiles~~ Watch out here.
~~reducers are nucleophiles~~

Vit C therefore acts as a reducer, or nucleophile
Oxygen acts as an oxidizer, or as an electrophile.

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As an example, what happens when iron and Oxygen combine?
ors

$Fe^{+2} + O^{-2} = FeO$ thus should be ferrous oxide

$2 Fe^{+3} + 3 O^{-2} \rightarrow \overset{2(+3)}{Fe_2}\overset{3(-2)}{(O)_3}$ thus should be ferric oxide

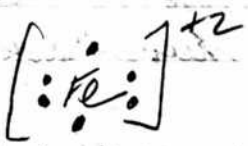
Is the above correct?

Oxygen is an oxidizing agent, ie an oxidizer.
It commonly exists in a state of -2

Elemental
Oxygen

Ok, easy to see.
This indicates an excess of electrons.
This is therefore a nucleophile.

Iron



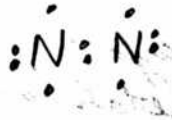
$[Ar]\, 3d^6\, 4s^2$

This would imply that Fe commonly has 6 electrons in its valence shell. Is this correct?

Now look @ O_2 in a gaseous form. O_2

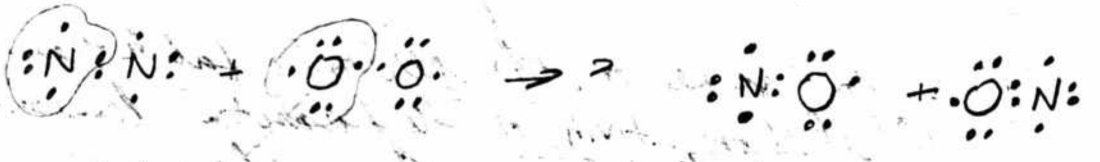
This is therefore an uncharged molecule.
But O likes to form two bonds.

FC = O(left) = 6-1-5 = 0 FC O right = 6-1-5 = 0.



Nitrogen likes to form 3 bonds.

FC (left) = 5-1-4 = 0 FC (Right) = 5-1-4 = 0



this looks to be highly reactive.
w/ a free radical.
(i.e. lone electron)

$2Zn \rightarrow 2Zn^{2+} + 4e^-$
$O_2 + 4e^- \rightarrow 2O_2^{-2}$
add
$2Zn + O_2 \rightarrow 2Zn^{+2} + 2O_2^{-2}$

So zinc net reaction is to donate electrons.
Oxygen net reaction is to gain electrons.
The metals therefore are nucleophiles
Oxygen is therefore an electrophile

Electrons are transferred from the zinc (metal) to the oxygen atom (non-metal).

Why & how? You know metals have lots of valence electrons that are ready to break away. This is why.

Fundamental question:

Are transition metals indeed nucleophiles?
It seems like they should be with the number of electrons buzzing around.

~~Well, this looks to be an interesting question, and it seems that you are quite right.~~

~~You can see this in numerous ways:~~
~~1. You know the transition metals have lot of potential valence electrons, thence one reason that they conduct so well.~~

~~2. You can see on the periodic table that the electronegativity of the transition elements is remarkably low. So another way of saying this is that the TM (transition metals) are "electropositive" instead of electronegative. Iron and Mg, for example, are even far less electronegative than Hydrogen !!~~

Be very very careful here!

Ok, we are getting there.

* A property of the transition metals is that they lose one or more electrons.

This means, therefore, that the transition metals are often subject to oxidation. This is the very definition of oxidation, the loss of electrons. The oxidation of a transition metal is caused by an oxidizing agent, or oxidizer, such as oxygen.

Take Fe^{+2}. This state means that it has lost electrons. The elemental form of Fe therefore would indeed seem to be a nucleophile, since it has the electrons to lose to begin with. But everything changes when it has been oxidized. Now it is electron deficient, and this would make it an electrophile. So the charge, or state of an atom or an ion is a critical factor in determining if something is a nucleophile or an electrophile. This looks to be a very important realization, therefore.

So Fe^{+2} is hardly the same as Fe or Fe^{+3}. These distinctions now become very important.

p991 Zumdahl & p992 is really helpful in understanding the character of the transition metals & their oxidation states.

ridiculous.

What you are seeing here is that it is ridiculous to speak in terms of electrophile and nucleophile w.r.t. transition metals (or anything else for that matter) unless you know what state it is in, ie oxidation state, which tells us how many electrons we have gained or lost.

So now we know Fe has a tendency to lose only 2 of the d electrons.
So elemental iron should look like:

~~com~~ possible

$\underset{S}{\ddot{\mathrm{Fe}}}$ or $\overset{s\,\&\,d}{:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Fe}}}:}$ Then the s & d orbitals combined (unconventional, but it makes sense)

Now, iron (and all the elements through zinc lose @ most 3 d electrons)
What he is really telling us is that the d orbitals get hard to remove. So for Iron:

We have Fe^{+2} = $\dot{\ddot{\mathrm{Fe}}}:$ but remaining d's are hard to remove

And when you have Fe^{+3} it is $\overset{d\ \text{left}}{\cdot\ddot{\mathrm{Fe}}\cdot}$ but remaining d's are hard to move
one d taken.

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Now lets go on to more interesting examples.
1. Some should use Oxygen straight forward
2. Some should not use oxygen
3. Some should be a partial loss and a partial gain of electrons. (Covalent bonds)

Sources used are Barrons Ez Chem p 258
Zumdahl p 164
Ch 6 Net paper from Coursera notes

Start out w/ Ez

1. Determine oxidation state of $\overset{2(+1)}{Na_2}\underset{(+6)(-8)}{SO_4}^{2-}$

This also shows you why a
polyatomic ion has the charge ~~that~~ it does.
It is not a mystery now...

2. Next is a given reaction:

$$\overset{0}{Cu}_{(s)} + 2\left[\overset{+1}{Ag}\overset{-1}{NO}_{3(aq)}\right] \rightarrow \overset{+2}{Cu}(\overset{(-1)\cdot 2=-2}{NO_3})_2 + 2\overset{0}{Ag}_{(s)}$$

So copper loses electrons (oxidized)
silver gains electron (reduced)
nitrate ion – no change.

Very good.

This equation in the book is not balanced. How do you get away with this?

*

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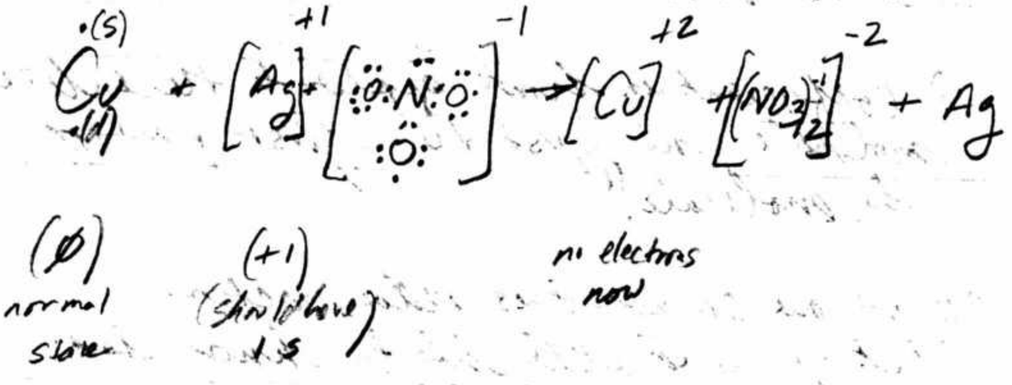
Now, Could you, out of curiosity, also draw a Lewis diagram for this reaction?



FC of left O:] 6-1-6=-1 This is where the charge on the nitrate ion comes from, the extra electron is on the oxygen side. Then what is going to allow the ionic bond of $AgNO_3$ to form. Although it does not really seem like an ionic bond as much as a coordinate covalent bond to me. What is ΔEN?

Ag = 1.93
O = 3.44

ΔEN = 1.51

This is very close to being ionic but not quite. Software determination. 26.45% says it is polar covalent.

What about Ag-N? 23.16%, polar covalent.
Not much difference there.

(1) Question: is Ag bonding to O here or N?
(2) What is the structure of silver nitrate?
It is Ionic. So what does this look like?

So in general, what do polyatomic ions look like?

I would like to know why this equation is not balanced.

a "2" in front of $AgNO_3$ means $2[AgNO_3]$

So I have balanced it now.

A coefficient in front applies to the entire molecule, not just the first part of the molecule.

Ok, we are OK with this redox reaction but you would still like to know what polyatomic ions look like and what is really bonding.

like, what does ~~$AgNO_2$~~ $AgNO_{3(s)}$ "look" like?

We see that in aqueous solution it exists as an ion.

look at an ionic bond:

$Na\cdot \quad \cdot\ddot{\underset{\cdot\cdot}{Cl}}:$

They join to make a bond.
$\Delta EN = 3.16 - 0.93$
$= 2.23$
≥ 1.7 it is ionic

What does this really mean & look like?
They apparently are not sharing but have transferred.
Transferred from where to where?
The Chlorine pulls it sharply, it is highly electronegative

Ionic bonds are electrostatic bonds.

Page 187

Ok, we are ok on EzChem level of redox: 258-260

Now let's move on to Zumdahl p164

Example given

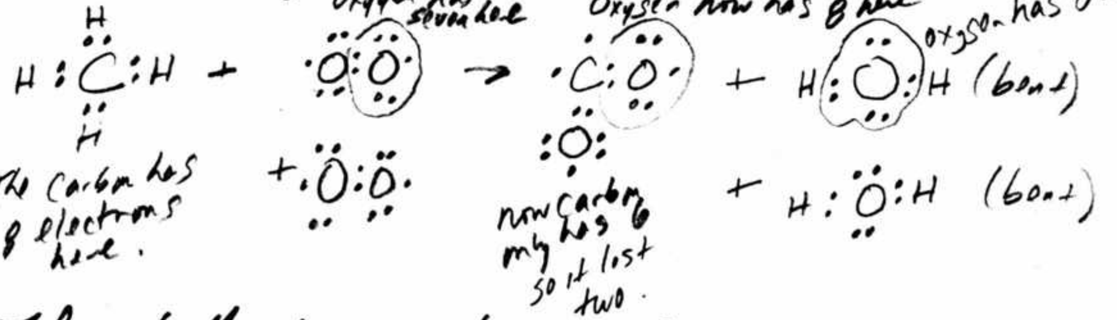
$$\overset{-4}{C}\overset{(+1)4}{H_4}(g) + 2\overset{\text{in its "natural" state } 0!}{O_2}(g) \xrightarrow{\text{add! heat!}} \overset{+4}{C}\overset{-4}{O_2}(g) + 2\overset{+2}{H_2}\overset{-2}{O}(g) + \text{energy}.$$

Notice what this shows: methane + oxygen create more CO_2 + energy.

but this require heat, this is a combustion reaction.

Ok, what happens?

Carbon is combining with oxygen so we know that carbon is being oxidized. But how do we show this?



This actually gets pretty bizarre. C can indeed have an oxidation state of +4 or -4 !!! even though our Spark table shows it having +2 or +4.

In this example

1. Carbon loses electrons. (So it is oxidized)
2. Oxygen "in its natural state" has an oxidation no. of zero
3. Oxygen therefore gains two electrons so it is reduced.

4. You can also see how partial transfers are taking place. Now it is more clear to see than w/ memorizing rules on oxidation states. Both methods should confirm one another.

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So anytime you have a transfer, or even a partial transfer of electrons (ie polar bond) you actually should be having a redox reaction.

This is an interesting way of looking @ reactions. Redox does not apply just to organic reactions.

Redox was an unexpected side route of study. It came about from the fuel cell reaction and the realization of lack of understanding as to what constitutes a redox reaction.

May 26 2015 Page 186

We are starting to learn about the energy of chemical reactions also. This is great. Already we have learned from Murray India that the equilibrium constant Keq is a useful indicator as to what happens. But then he also talks about ΔG being exothermic (it's negative! because it lost energy) and endothermic - positive, because it gains energy. We have not learned to compute it yet but we also already know that both of these approaches have been combined mathematically into a single relationship. This is really very cool and it is the same relationship that Davis was talking about in his organic chemistry book.

So now we continue w/ Murray India

We are not using the relationship formula yet. The focus now is on

$$\Delta G = \Delta H^{\circ} - T\Delta S^{\circ}$$

the °'s mean std temp & pressure.

↑ enthalpy (usually the dominant term) (endothermic or exothermic) (positive, ie gains heat) (negative, i.e., loses heat)

↑ entropy (disorder)

more disorder is positive splitting up into two is an example of more disorder

Now, this is a great section conceptually, from p 122-127 & I would not trade it for anything, but how do you apply it? (Cont)

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He ends up being very lazy on us with the question set.
He (Murray) only gives us generalized questions and
avoids the details of how we acquire ΔG, ΔH etc.
Apparently the value of an example on p 123
can be acquired from tabulated sources, but he
avoids that need entirely. For now, we will go
along w/ the program, but I would like to know
how to acquire these values since that is the real
world need.

For now, let's go after the generalized questions.
We have covered $K_{eq} < 1$ and $K_{eq} > 1$
and we have covered $\Delta G < 0$ and $\Delta G < 0$
and $\Delta G = \Delta H + T\Delta S$
where ΔH is usually the dominant term
of "enthalpy" which refers to the gain or loss of
energy in the reaction, ie exothermic or
endothermic.

Now the questions

OK ✓ 5.10 Which is more favored energetically?
$\Delta G = -44$ KJ mol or $\Delta G = 44$ KJ/mol?

Answer: -44 KJ mol (energy lost)

OK 5.11 Which is more exergonic (exothermic)
$K_{eq} = 1000$ or $K = .001$

Answer $K_{eq} = 1000$

→ no you cannot do this yet!

5.12 Which reaction is faster? NO! - It is not ΔG It is $\Delta G^{\ddagger}$!!!

$\cancel{\Delta G}$ = +45 kJ/mol or $\cancel{\Delta G}$ = 70 kJ/mol

NO! Wrong

Interesting question. They both require energy be put into the system for the reaction to occur. The second one, 70 kJ/mol has more energy being put into the system so I think that it is faster..

Answer: 70 kJ/mol

Lets see how we did.

I missed the last one. Let's see why. Answer is that a lower ΔG is faster - why?

What we see here is that on p124 he really did not give any examples on the rate question from a numerical standpoint. So I ~~see~~ still do not see how I would know that

UH YOH! Guess what? It is not ΔG he is using in the problem. It is $\Delta G^{\ddagger}$ "dagger dagger"! That is entirely a different story then and he did not yet explain rate of reaction from a numerical standpoint. We have:

OK ① Equilibrium - in what direction does the reaction proceed?

OK ② Is the reaction exothermic or endothermic?

we don't know yet! ③ How fast does the reaction proceed?

We now can proceed, leaving aside the rate question for the time being, and go on to the next topic, and a very interesting one at that, of Bond DISSOciation Energies.

We have looked up & settled the issue of
dissociation vs ~~dissa~~ disassociate
and the answer is:
that they are both <u>valid</u> terms
but we also see that dissociate is clearly preferred in the chemistry profession.
So the lesson is:
Choose your weapons accordingly.

Separate topic before we proceed.

We understand clearly now why iron Fe^{+2} binds to oxygen

Fe^{+2} O^{-2}

guess what
straightforward in the
logic of bonding.

Fe^{+3} O^{-2}

Not so logical and we need to form
Fe_2O_3
and this required a higher energy state in iron.

Also citrate is, guess what, -3 charge.
So guess why it bonds to Fe^{+3}.

Bonds forming & breaking & their relationship
to exothermic and endothermic reactions

Back to Murray - India p 125

1. Heat is released when a bond is formed.
This IS a negative ΔH, an exothermic reaction

2. Heat is absorbed (positive ΔH) when a bond is broken: This is endothermic

He says we know this from the previous discussion, but I do not see how we actually knew this declarative statement w/ any conviction based upon the prior discussion. He did say if ~~something is~~ a reaction is exothermic (ΔH is negative) then the "~~products~~ bonds are more ~~stable~~ stronger and more stable

So somehow he has made the connection, that I did not, that

* a bond that is stronger and more stable is also by deduction a bond ~~that~~ has therefore been formed, and that the process is positively accompanied by a release of energy, that ΔH is negative (loss of energy) and ~~that~~ it is an exothermic reaction. !

* This is one powerful statement along with the converse that energy is absorbed (positive ΔH, endothermic, the bonds are weaker in the products than the bonds in the reactants) in the reaction when bonds are broken

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These are very important statements that are being made here. Lets now go to an example given.

Example:

A reaction occurs that breaks reactant bonds with a total strength of 380 kJ/mol.

The products form bonds that have a total strength of 400 kJ/mol.

First, he tells us that ΔH for the reaction is −20 kJ/mol, therefore it is exothermic.

This tells us therefore, that

ΔH = Strength of Bonds in Reactants that are broken − Strength of Bonds that are formed in the products.

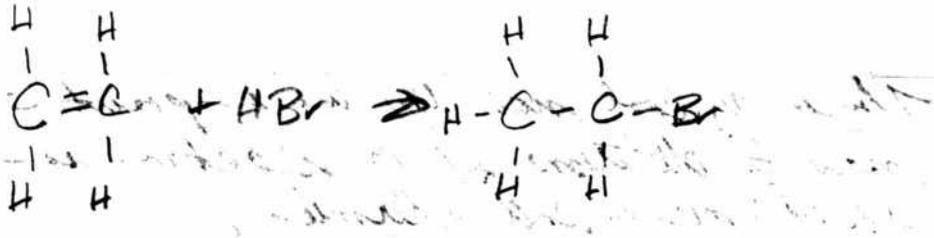
so

380 kJ/mol − 400 kJ/mol = −20 kJ/mol

Now, lets look @ the example further

Ez Chem has a bond table p 205

Bond Tables: EZ Chem p 295
Murray India p 125



Start:
4 CH Bonds = 4(413) = 1652
1 C=C = (1)(614) = 614
Σ 2266
HBr = 363 +363 = 2629 KJ/mol
Now try products:

CH 5(413) = 2065
C-C 1(347) = 347
C-Br ≈ 293? = ~293
Σ = 2705

Reactants - Products = 2629 - 2705 = -76 kJ/mol

* The bonds of the products are therefore stronger & more stable
ΔH is, by definition, the change in bond energy
it is also the change in enthalpy
but change in bond energy is easier to remember.

We get - 76 kJ/mol
He lists: -84.1 kJ/mol
That is great. We are right on track.
This is not the free energy change, it is only the bond energy change but this is usually the dominant term.

It is an exothermic reaction regardless of the influence of entropy.

I have done well.

This is very cool now. You are in position now to determine if a reaction is exothermic or endothermic.

What is most interesting to me in exothermic or endothermic is that an exothermic reaction results in stronger and more stable bonds.

* This is profound to me because it indicates if the reaction is the preferred state in nature or not.

* Conversely an endothermic reaction has less stable and weaker bonds. He directly says this on p 124 Murray India.

These are the major implications from ΔH determination, this is really neat process. This is really powerful knowledge to apply.

Another example: $H_2(g) + Cl_2(g) \rightarrow 2HCl$

(i) H-H = 432 H-Cl = 427

1 Cl-Cl = 239 2(427) = 854

ΔH Σ = 671 kJ/mol

Reactants ΔH Products

so ②

671 - 854 = -183 kJ / moles

Conclusions:

Not done

$\frac{-183}{2}$ = -91.5 kJ per mole.. remain exothermic

1. An exothermic reaction.
2. Product bonds are stronger & more stable the reagent bonds.

for the next section, in p126 he is trying to explain more thoroughly the relationship between exothermic reaction & stability of the products.

Statement:
1. Making product bonds releases heat
2. Breaking reactant bonds absorbs heat.

I am really not sure how I would know this. He says it is so, but I am not connecting w/ it yet. Seek an alternative explanation of why this is the case.

But for now, we are willing to accept that exothermic reactions result in stronger and more ~~stables~~ stable bonds.

Let us see if we can find another interpretation for statements 1 & 2 above.

See p. 369 Zumdahl also.
"Without the consideration of individual bond energies, chemistry would be overwhelmingly complex"!

Murray has given us a great example of the importance of bond strength of P–O in relationship to ATP and energy production on p 126.

The P-O bond question that came to mind of Murray's example on p 126 was a very worthy question.

It ends up that bond energies are only AVERAGE values and that they can and do vary considerably. They are indeed affected by their surroundings & surrounding bonds.

The concept of an "average" bond strength, however, remains very useful.

The example of ATP P-O bond by Murray p 126 was an excellent demonstration how a bond strength, in this case the P-O bond, can vary considerably depending upon its surroundings and adjacent bonds.

I wonder what Phosphorus bonding looks like?
Should be [Ne] $3s^3 3p^3$
Should have 6 valence electrons.
But apparently P can form 5 bonds commonly
So I have no idea how I would have predicted this.

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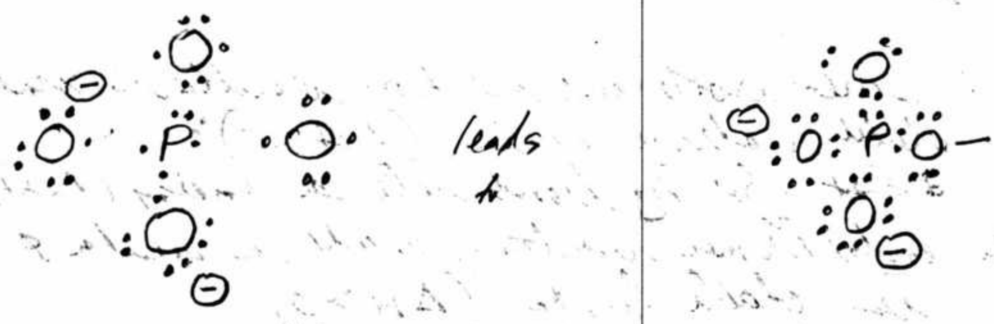
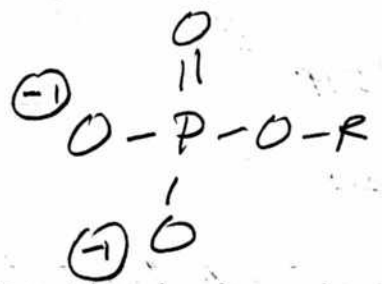
Looking @ P bonds in Murray p126 we have:



This shows us that Phosphorus has 5 valence electrons, not 6 as the electronic configuration might suggest.

There is also a reason that we expect to see 5 bonds w/ phosphorus. Lewis diagrams really do help you in many cases to understand & ~~interpret~~ what happens.

So the phosphate group, as determined by the Lewis structure is



$$^{\ominus}O-\overset{\overset{O}{\|}}{\underset{\underset{O^{\ominus}}{|}}{P}}-O-R$$

which is exactly what Murray - India ~~has~~ is showing on p 126.

and this particular section of the molecule has a charge of -2. You also know that this make the segment electrophilic.

So you are carrying forward from these section that

1. net exothermic reaction results in more stable & stronger bonds. ($\Delta H < 0$)
   & that forming bonds release energy (heat)
2. endothermic reaction result in weaker & less stable bonds ($\Delta H > 0$)
   & that breaking bonds absorbs heat

And I see that you should be able to remember this.

But I still am not sure if I exactly understand why. These are powerful statements in Chemistry & Murray says so.

But why is this the case?

There is another way of interpreting this that is more straightforward and that is inherent in the definition of ΔH itself.

From Zumdahl p374

ΔH is *defined* as:

ΔH = energy required to break bonds − the energy released when bonds form.

We can now actually see the inherent logic within the definition and for the assignment of positive and negative degrees to the equation.

The natural order of entropy explains this equation. We know that nature seeks its simplest & least energetic state. (Nature trends toward disorder). So we know the end result of any natural reaction is to form simpler & more stable bonds. Example $C=O$ and $C=C$ bonds trend toward $C-O$ and $C-C$ bonds. When this happens, the energy inherent w/in the more complex bond arrangement had to go somewhere and therefore it had to be _released_. Note that the bonds being formed are actually simpler in structure and generally of lower energy. Also the original bonds had to break to begin with and this requires energy also.

So, think about how you would construct a definition. You could start with the energy inherent in the system & compare that to the energy when you finish or visa versa. $\Delta H =$

The former approach ie Start _to Finish_ has been adopted and this actually makes perfect sense. It is a definition that we had to choose something

$\Delta H =$ Start − Finish

Start	Finish
Energy required (I think energy inherent at the start is a logical interpretation) to break (existing) bonds	Energy released (I think energy _inherent_ at the finish is a logical interp) when bonds form.

Zumdahl p372 explains the process even further.

I have to say I really do like my interpretation.

"Energy inherent" in the system, either start or finish, is what makes sense to me. Then we simply define the difference ΔH as

REQUIRED		RELEASED
ΔH = Starting "inherent" energy	−	finishing "inherent" energy
(ie, required when bonds (of a more complex and unstable nature) break)		(ie, released when bonds (albeit simple & more stable) form)
this term dominates in endothermic reactions.		this term dominates in exothermic reactions

Comprehensive bond dissociation tables are are very valuable source of empirical data.

Continued from May 23 2015

Accomplishments

And, I think, therefore

that this is a very sensible
place to end Vol IX.

Our list of accomplishments continues however.

23 Is familiarity with energy and
equilibrium constants of reactions

Keq
ΔG
ΔH
activation energy
exothermic or endothermic

This knowledge tells a lot about if a
reaction is likely to occur or not
and how fast it will occur.

24. We have the flame spectrometer and the
flashlight projects to take on
in addition to the biofield sensor.

25. The oxidation of blood and the associated
energy loss has now been successfully
and reasonably modeled. It may be of
interest to empirically test the model.

(CONT!)

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26. A mechanism of disruption in the protein myoglobin by the CDB has been identified. P1019-1020 Zumdahl. The CDB is allowing the oxygen bridge to form and is therefore oxidizing the blood to the Fe+3 state. This is crucial information