Oxidation State & Oxidation of Alcohols

2/1/2023

Calculating Oxidation States (12.4)

Formal charge: method of keeping track of e^-.

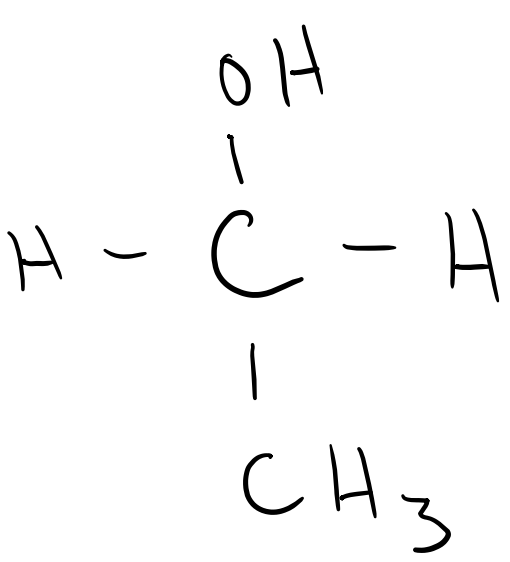
Does not consider electronegativity (considers all e^- shared equally)

"VUSF"

	Carbon
Valence	4
− unshared	− 0
− ½ shared	− 4
Formal charge	0

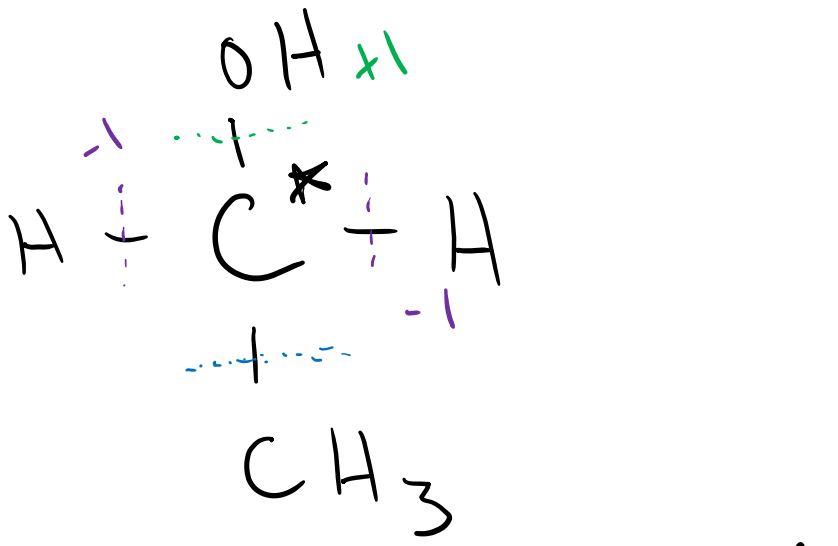
Oxidation state: different method which does consider bond polarity (unequal sharing of e^-)

- a bit more precise notion of relative e^- richness & therefore reactivity!



- Carbon w/ 4 bonds always has zero formal charge!
- ox state could be −4 to +4!

Calculating Oxidation States (typically for Carbon) (12.4)



-1 -1 +1 = $\boxed{-1}$*

EN:

H < C < Br < N ~ Cl < Oxygen

1) Bonds to atoms w/ same EN can be ignored. (other carbons)

2) +1 for each bond to more EN atom (O, N, X)

3) -1 for each bond to less EN atom (H)

4) add formal charge of atom (if it has one) (usually won't)

Oxidation and Reduction (of Hydrocarbons)

END OF QUIZ 2 material

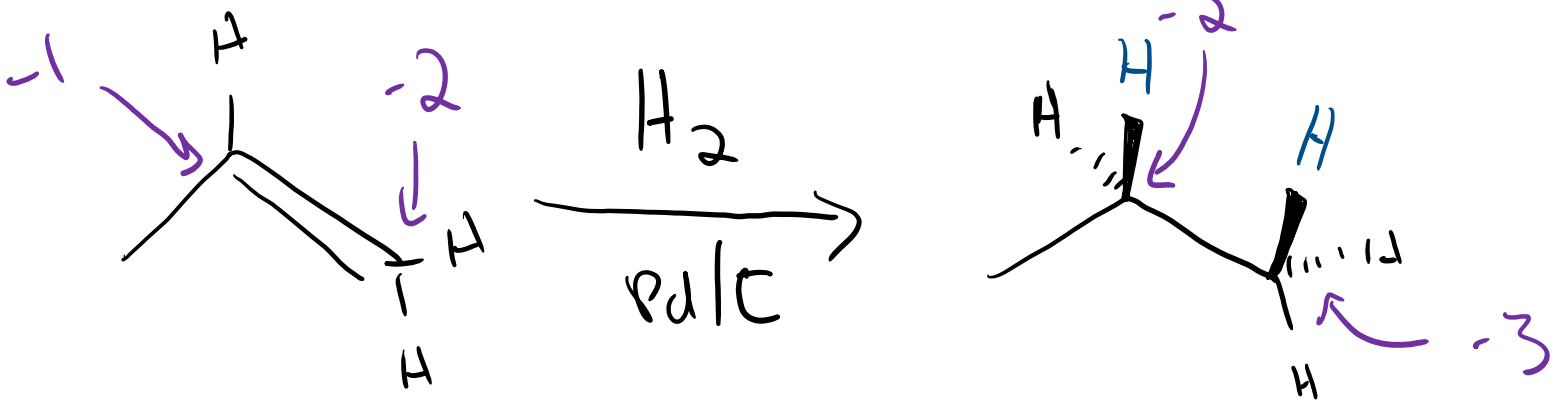
Oxidation is the loss of electrons. (OIL)

Oxidizing an atom increases its oxidation state. (more +, since losing e⁻)

% H ↓ and/or % O ↑ for oxidation

Reduction is the gain of electrons. (RIG)

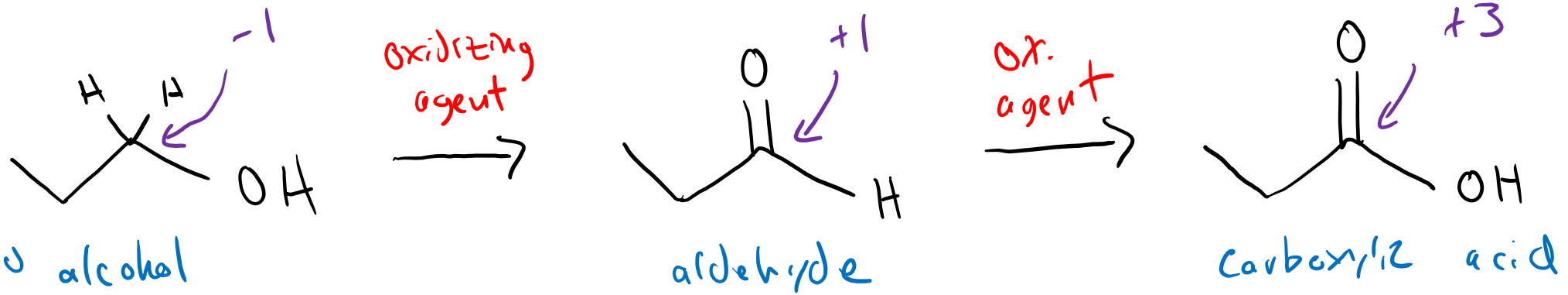
Reducing an atom decreases (reduces) its oxidation state. (more -, since gain e⁻)



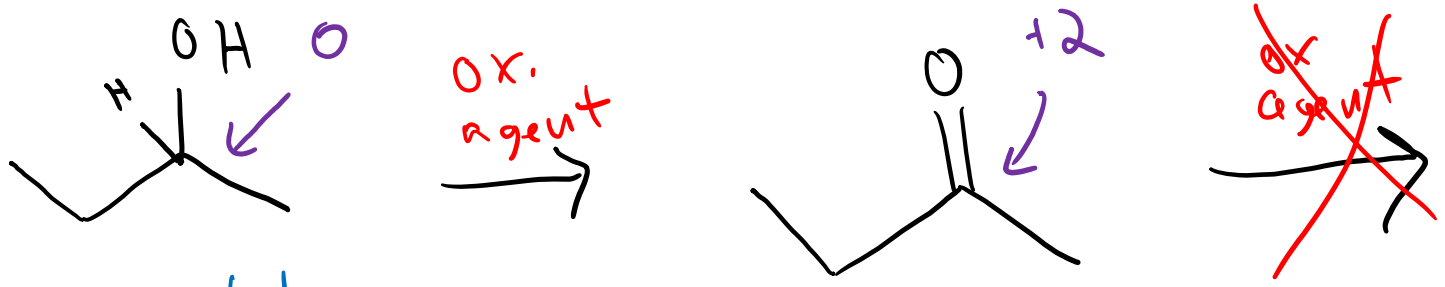
% H ↑ and/or % O ↓ for reduction

Oxidation States and Functional Groups

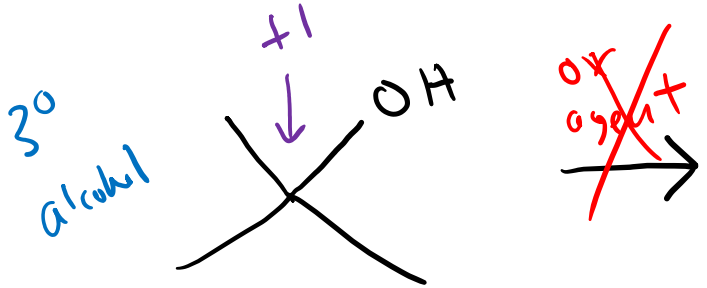
(12.10)



1° alcohol — aldehyde — carboxylic acid



2° alcohol — ketone

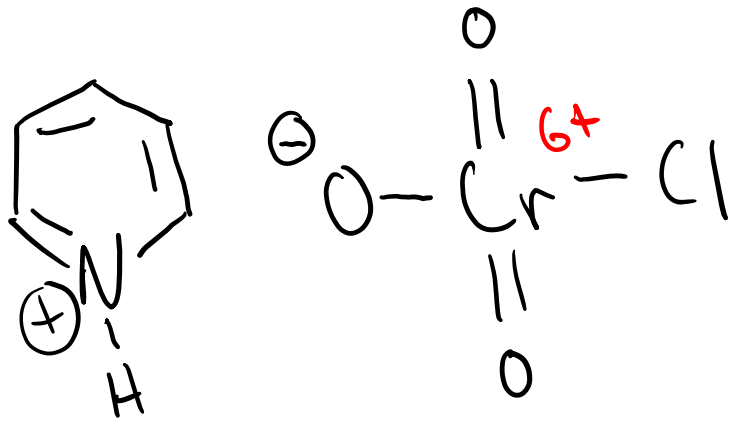


overall trend:

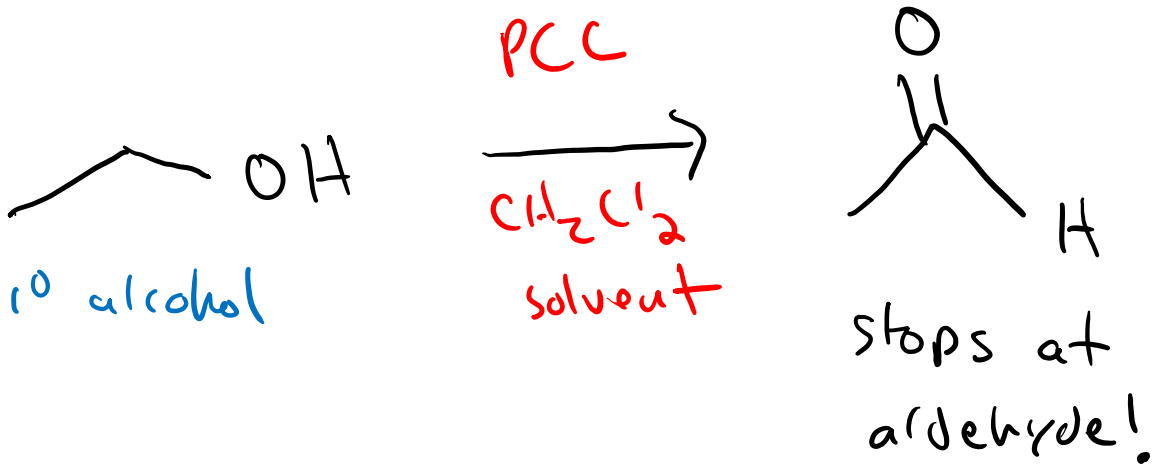
can only oxidize once per C-H bond on a given carbon

Chromium-based Reagents for Oxidizing Alcohols (12.10)

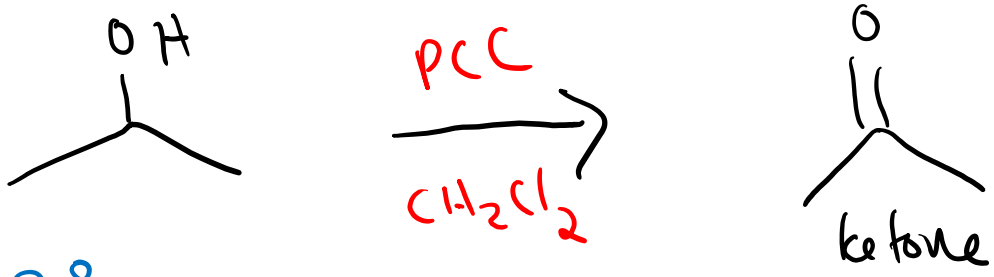
pyridinium chlorochromate



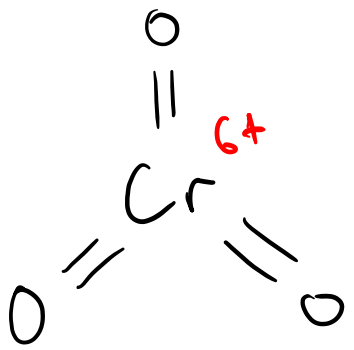
aka "PCC"



- requires anhydrous conditions - absolutely no H_2O! (CH_2Cl_2 solvent)
- extremely toxic + carcinogenic



Chromium-based Reagents for Oxidizing Alcohols (12.10)

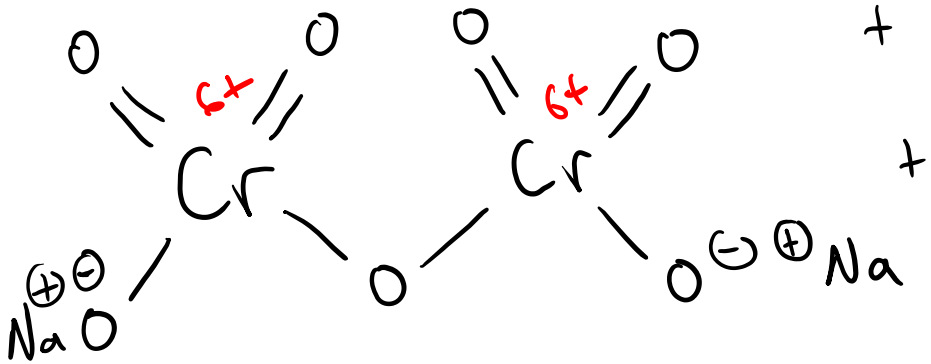


+ H_2SO_4

+ H_2O (aqueous)

"CrO_3" aka Jones reagent

or



+ H_2SO_4

+ H_2O

$Na_2Cr_2O_7$

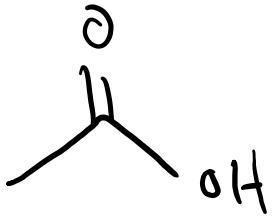
sodium dichromate

1° alcohol

CrO_3

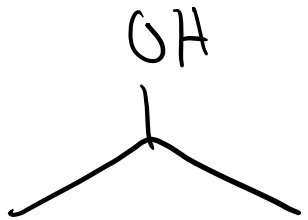
H_2SO_4

H_2O



carboxylic acid

(not aldehyde)



CrO_3

H_2SO_4,

H_2O

ketone

Crocoite – natural source of Cr^{6+} (not on exam)

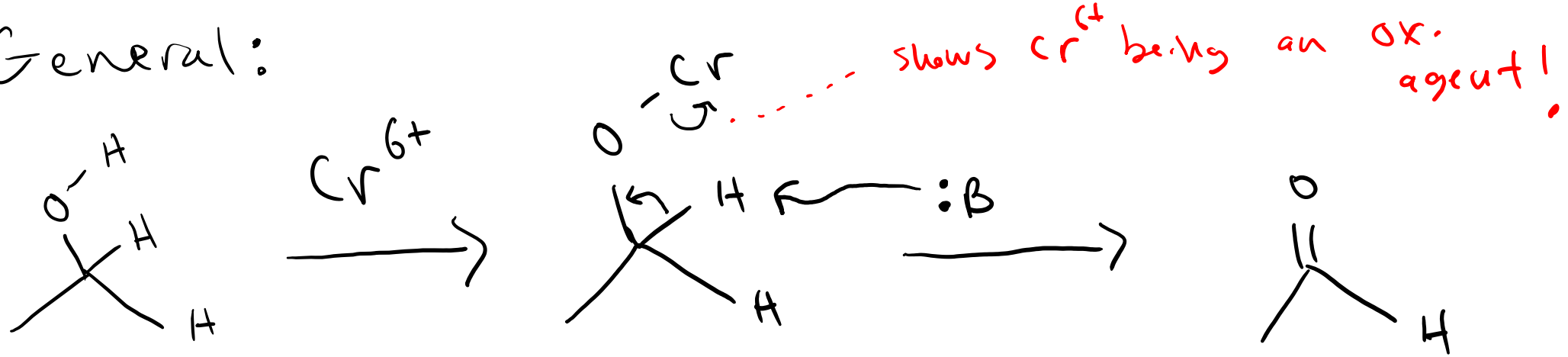
+2 +6 -8
$Pb^{+2}CrO_4^{-8}$

The original “schoolbus yellow” paint pigment was also $PbCrO_4$ 😬

(but not anymore)

Oxidizing Alcohols with Chromium: Mechanism

General:



E2!

PCC:

Oxidizing Alcohols with Chromium: Mechanism

Aqueous Cr^{6+}: