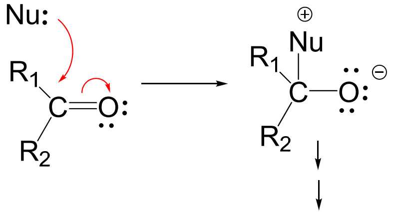
A/K II

Nucleophilic Addition Rxns

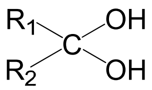
- General
- Hydration

Ref	16: 6
Prob	rewrite mech.'s
Adv Rdg	16: 7

General

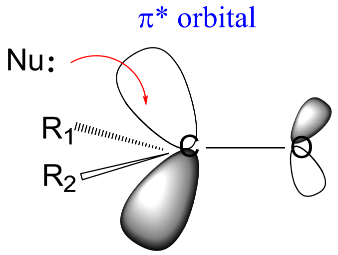


(e.g.,



"Hydrate")

3-D Picture



N.B.

Nu comes in from "left",

attacking the empty π*
at a 45° angle to the sp^2 plane

either from top or bottom

General ...

Reactivity (kinetics) increases if

- δ^+ is large

  (*electrostatic attraction increased*)

- R_1 , R_2 small

  (*approach by Nu easier*
  b/c less "steric hindrance")

More Comments on Reactivity (kinetic)

1.) Aldehydes more reactive than ketones.

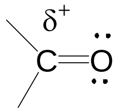
a.) "H" smaller than "alkyl"

(*Nu approach is easier*)

b.) "alkyls" mildly e^- donating,

(*due to hyperconjugation*)

reduces δ^+ on



∴Nu: attracted less; rxn rate ↓ ;

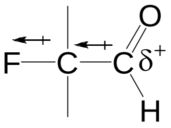
ketones react slower

reactivity ...

2.) Presence of "Inductive EWG"

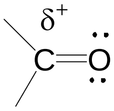
(*esp. F, Cl on* α *C*)

e.g.,



increases reactivity

increases δ^+ on



∴ more reactive towards Nu:

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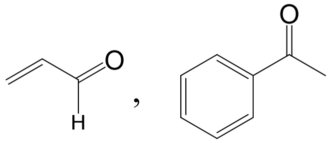
reactivity ...

3.) Conjugated (incl. aromatic) Carbonyl Cmpds.

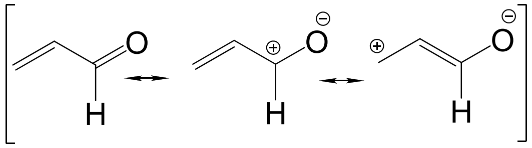
e.g.,



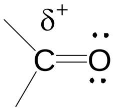
less reactive due to:

"resonance" or "delocalization" of δ^+

Ex.:



δ^+ not concentrated on



Reactivity (Thermodynamic)

More or less parallels Kinetic Reactivity;
(*general observation, not always true*)
i.e., if a carbonyl cmpd. reacts fast,
its product will be more stable.

Rationalization:

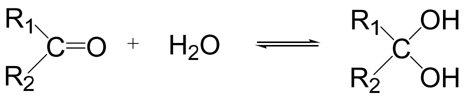
1.) Small R groups favor add^n products, since the tetrahedral arrangement of the adduct causes crowding which is not a problem for small R's

2.) The dipole nature of a C=O π bond is strongly affected by EWG's, EDG's and resonance effects.

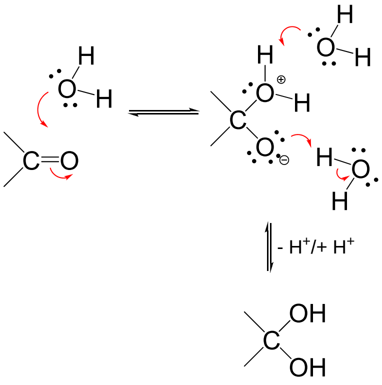
In particular,
EWG's strongly increase the polarity of a C=O π bond (*much more so than that of a C-O* σ *bond*) thereby de-stabilizing the carbonyl structure (*and facilitating form*^{n} *of the tetrahedral add*^{n} *product which has only* σ *bonds*)

Hydrate Formation (Add^n of H_2O)

Overall:



Mech.



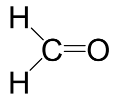
Equilibrium! mostly on left

except when : R_1, R_2 small (e.g. = H), or

R_1, R_2 have inductive EWG's

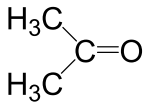
Examples

when dissolved in H_2O

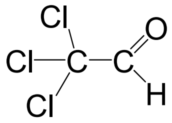


"formalin"

mostly hydrated



poorly hydrated



"chloral"

mostly hydrated

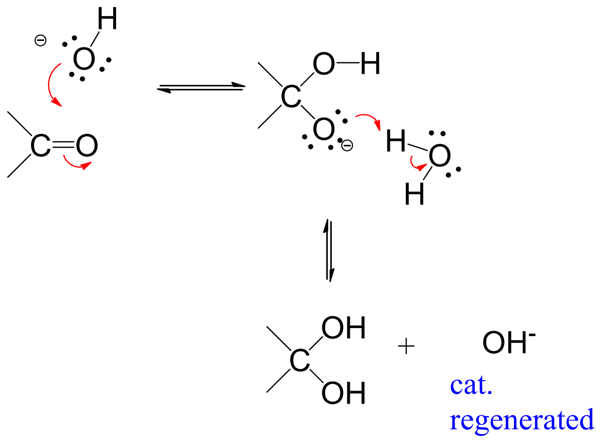
Acid/Base Catalysts

- In neutral medium (pH ≈ 7)

  rxn (=establishmt of equil.)

  is slow
- rxn rate can be increased in
  - base (high pH), b/c stronger nuleophile
  - acid (low pH), b/c substrate is activated

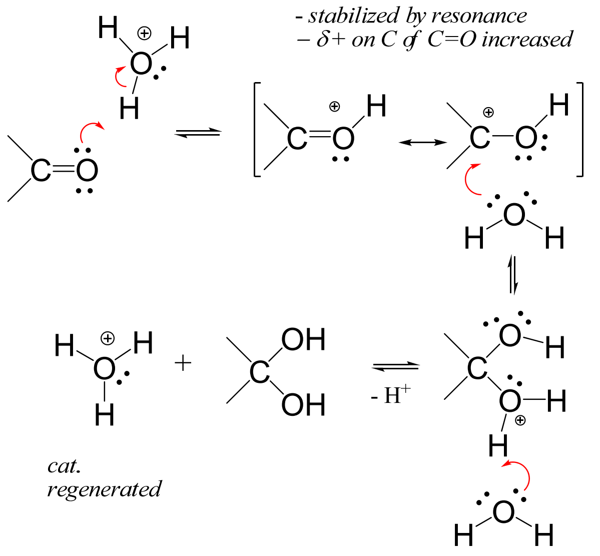
Base Catalysis



cat.
regenerated

- OH^- is stronger Nu: than H_2O
- attacks faster ....

Acid Catalysis



- *stabilized by resonance*
– *δ+ on C of C=O increased*

- H+

cat.
regenerated

N.B.

H^+ (or H_3O^+) increases pos. charge on carbonyl C;

causing greater attraction;

increasing rate!