A/K II

Nucleophilic Addition Rxns

- General
- Hydration

Ref 16: 6

Prob rewrite mech.'s

Adv Rdg 16: 7

General

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

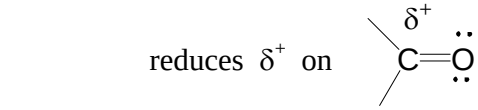
- (*electrostatic attraction increased*)
- (*approach by Nu easier*
  b/c less "steric hindrance")

More Comments on Reactivity (kinetic)

1.) Aldehydes more reactive than ketones.

a.) "H" smaller than "alkyl"
(*Nu approach is easier*)

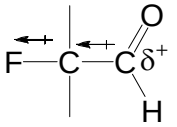
b.) "alkyls" mildly e^- donating,
(*due to hyperconjugation*)

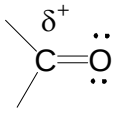
reduces δ^+ on 

reactivity ...

2.) Presence of "Inductive EWG"

(*esp. F, Cl on α C*)

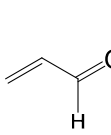
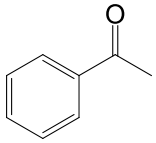
e.g.,  increases reactivity

increases δ^+ on 

∴ more reactive towards Nu:

reactivity ...

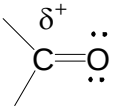
3.) Conjugated (incl. aromatic) Carbonyl Cmpds.

e.g.,  , 

less reactive due to:

"resonance" or "delocalization" of δ^+

Ex.:

δ^+ not concentrated on 

Reactivity (Thermodynamic)

More or less parallels Kinetic Reactivity;

(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.

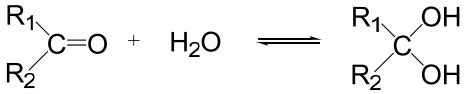
2.) The dipole nature of a C=O bond is
strongly affected by EWG's, EDG's
and resonance effects.

In particular,

EWG's strongly increase the polarity
of the C=O bond,
de-stabilize the molecule and
facilitate form^n of the tetrahedral add^n product.

Hydrate Formation (Add^n of H_2O)

Overall:



Mech.

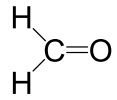
Equilibrium mostly on left

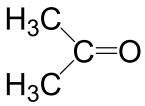
except when : R_1, R_2 small (e.g. = H), or

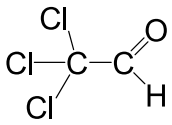
R_1, R_2 have inductive EWG's

Examples

when dissolved in H_2O







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

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

Acid Catalysis

N.B.

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

causing greater attraction;

increasing rate!