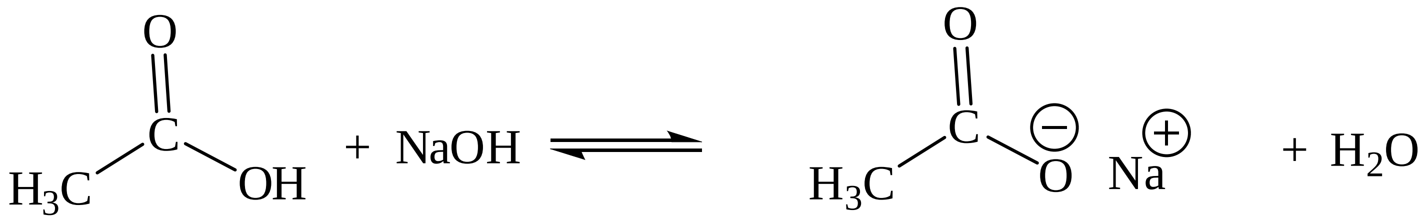
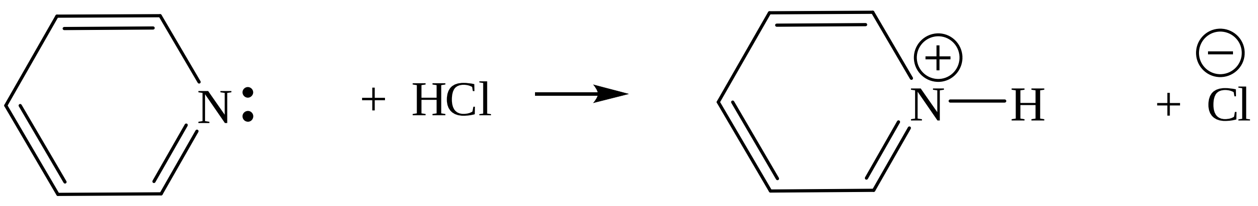
Reaction Types

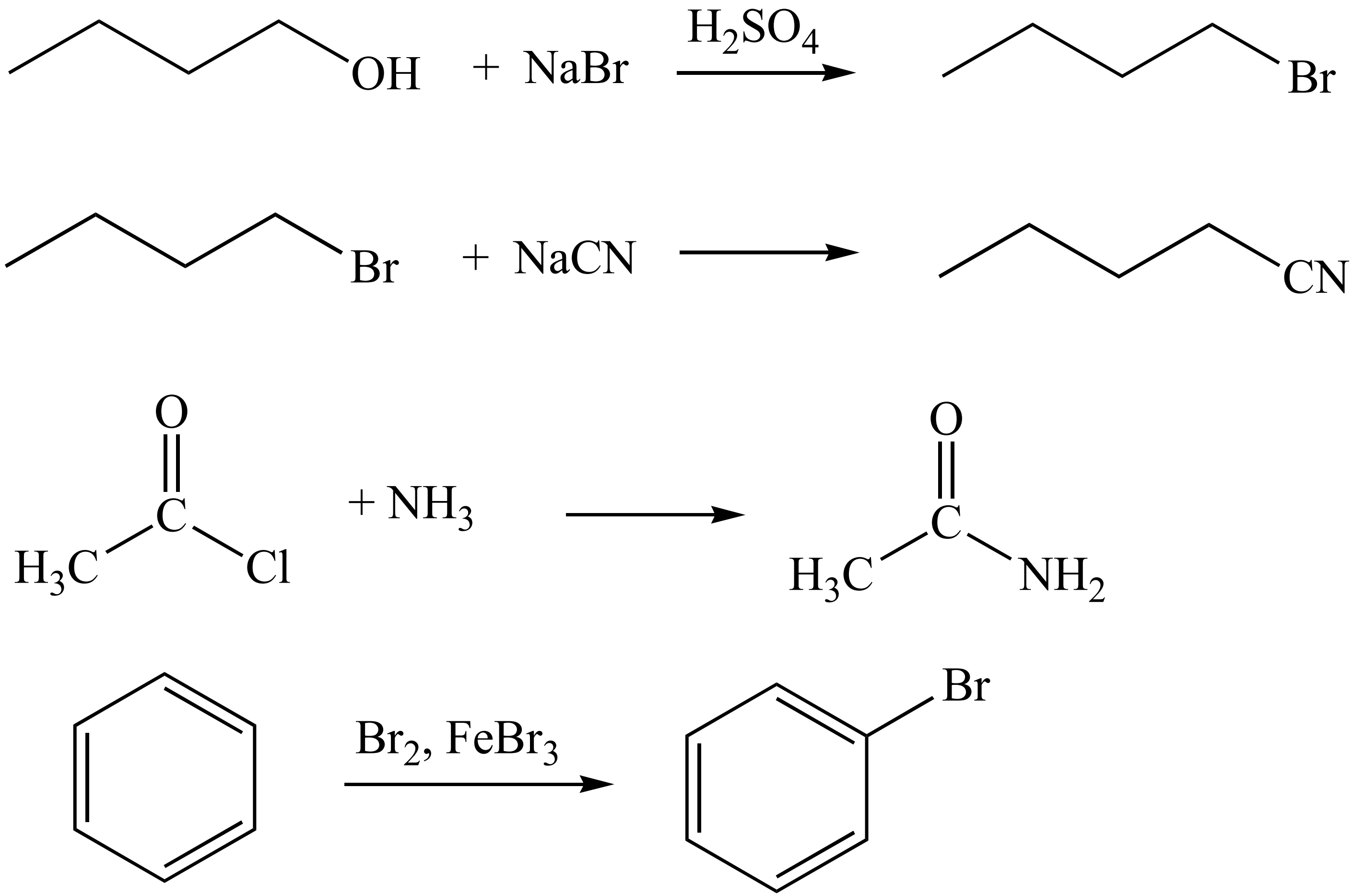
Proton-transfer reactions...





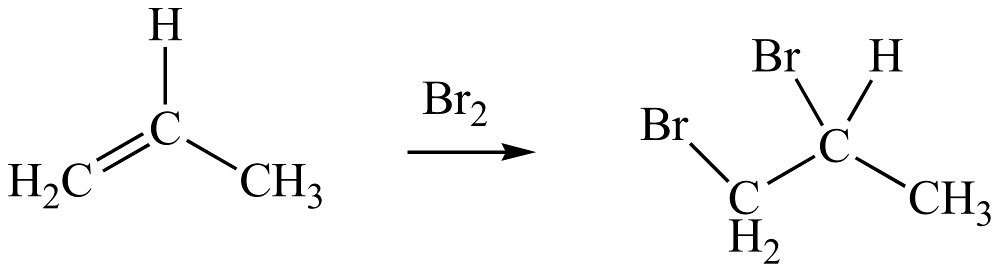
Reaction Types

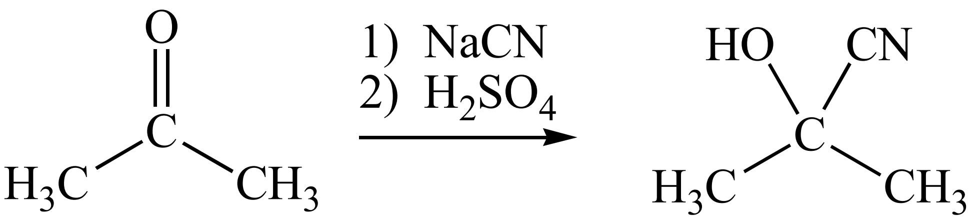
Substitution



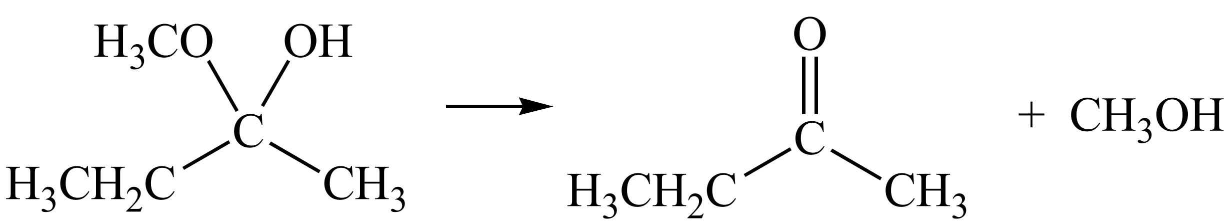
Reaction Types

Addition Reactions ...to a pi bond.



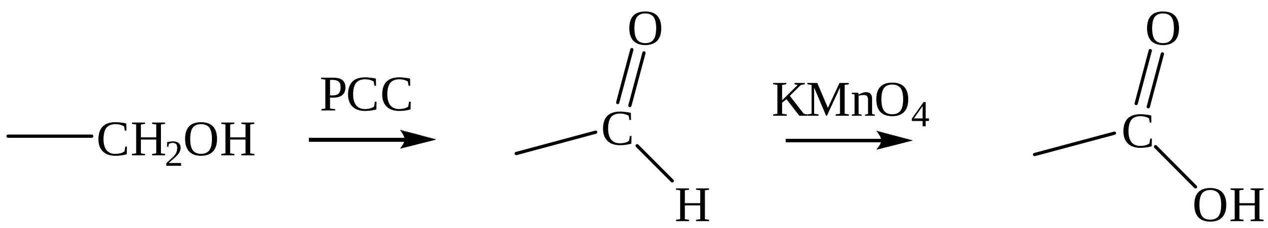


Elimination Reactions ... the reverse of addition, forms a pi bond.

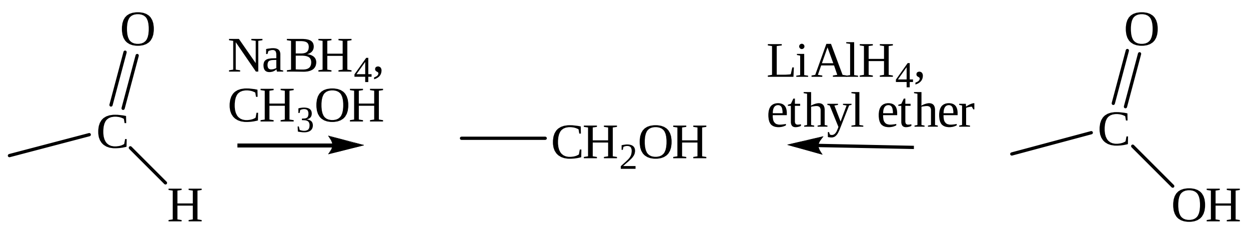


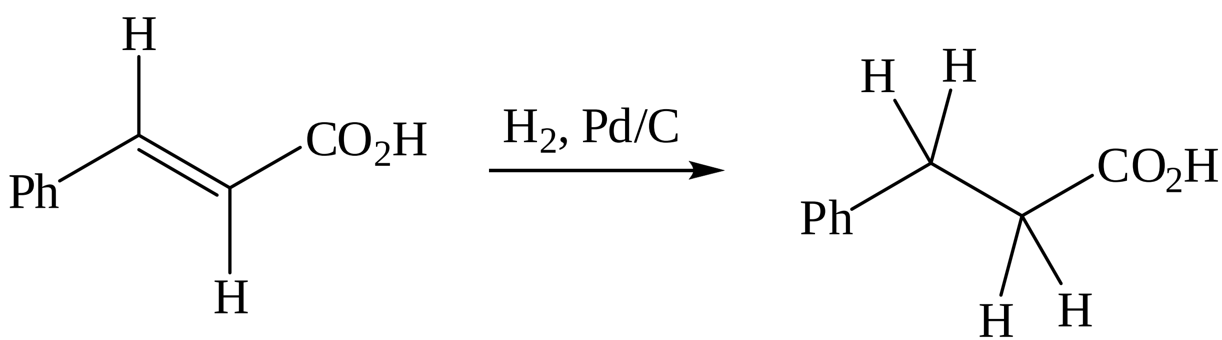
Reaction Types

Oxidation ...the addition of O or removal of H_2



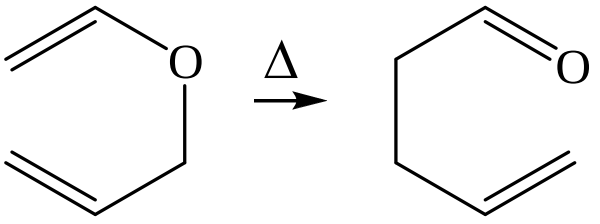
Reductions ...the addition of hydrogen, H_2

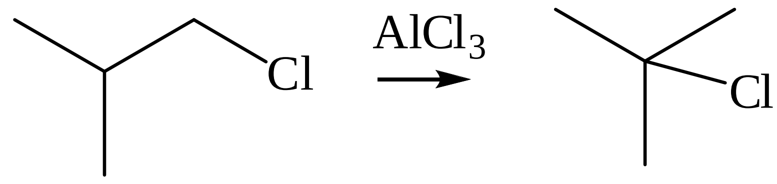




Reaction Types

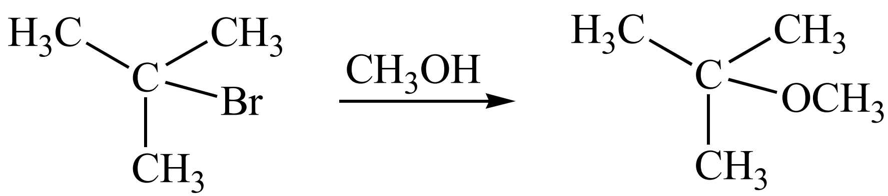
Rearrangements

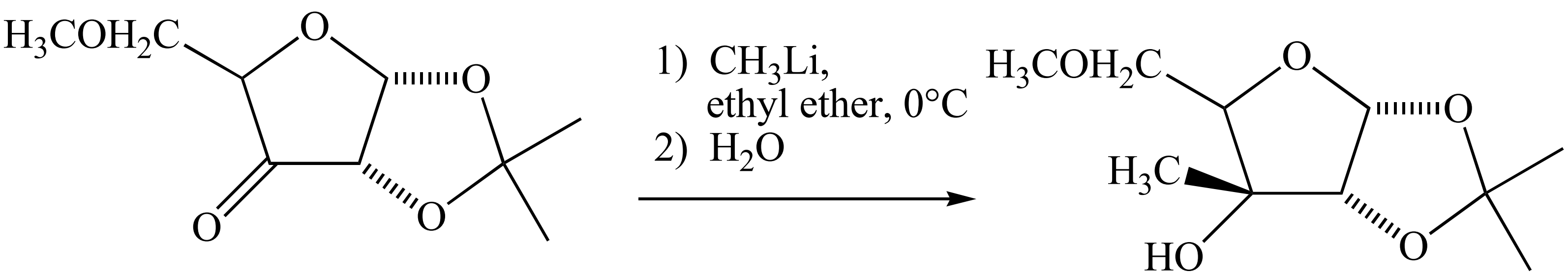


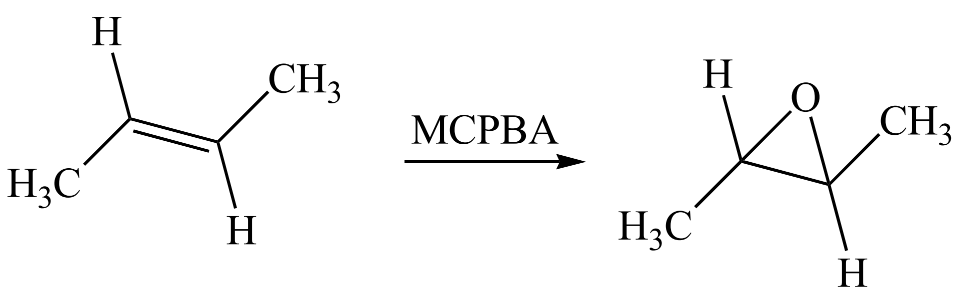


Reaction Types

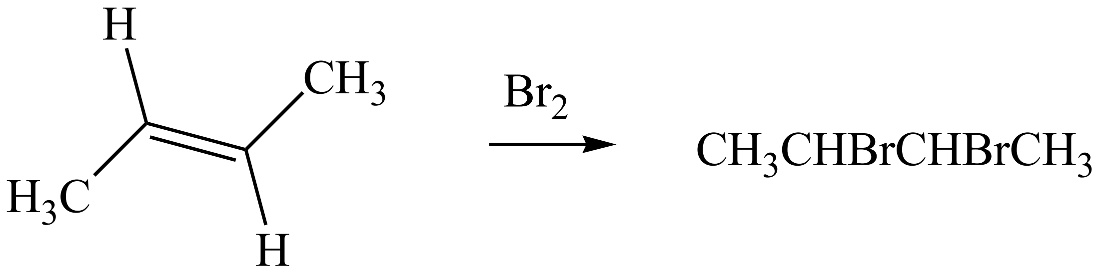
Practice!

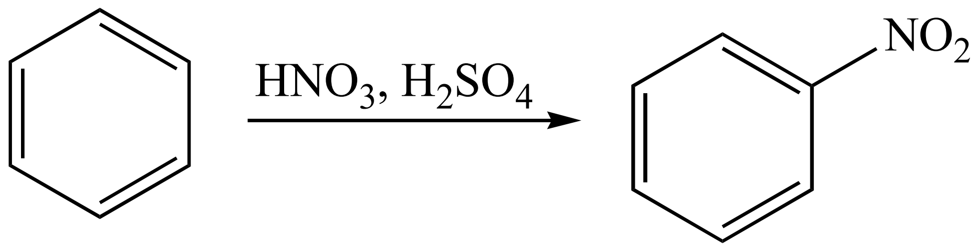


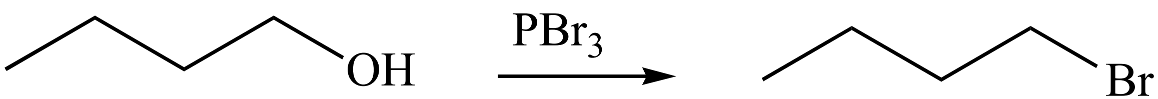


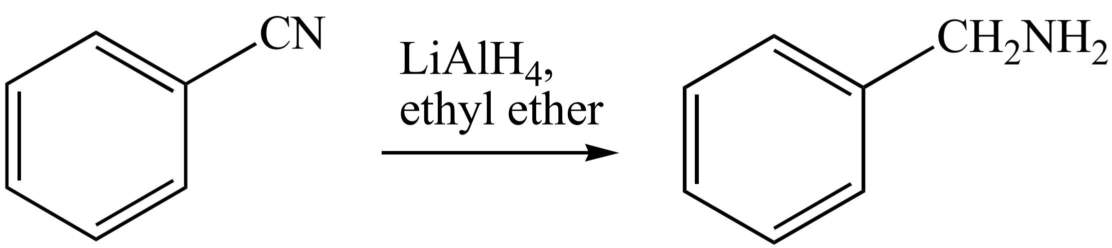


Reaction Types









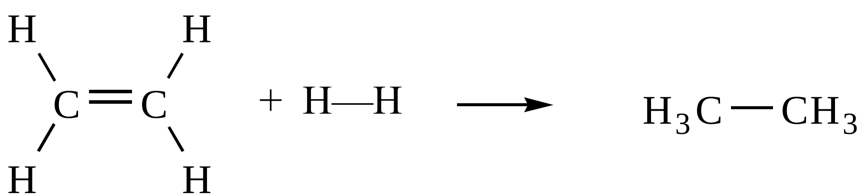
Thermodynamics

Enthalpy - ΔH ...

$\Delta H°_r$ can be approximated by using...

Bond energies: $\Delta H°_r = \Sigma$(bonds broken) - Σ (bonds formed)

For example:



$\Delta H°_r$ = (C=C + H-H) – (2 x C-H + C-C)

= (611 + 437) – (2 x 414 + 347)

= -127 KJ/mol

Reactions in which the products have stronger than the reactants will tend to have…

Thermodynamics

Entropy - ΔS

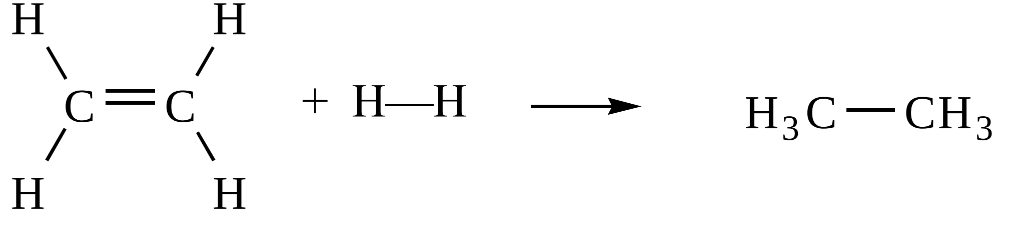
•Entropy is a measure of... disorder.

•Gases have more disorder than liquids and solutions, liquids and solutions more disorder than solids.

•$\Delta S°_r$ is positive for processes that involve an increase in disorder and negative for processes that involve an increase in order:

$$H_2O\,(s) \longrightarrow H_2O\,(l)$$

$$CH_3OH\,(l) + SOCl_2\,(l) \longrightarrow CH_3Cl\,(g) + SO_2\,(g) + HCl\,(g)$$



Thermodynamics

- <u>The Second Law of Thermodynamics</u>: For any spontaneous process, the entropy of the universe will increase.

As applied to chemical reactions, for any product-favoured process, the entropy of the universe will increase.

The entropy of the universe is increased by:

- an increase in entropy within the reaction
- the release of heat from the reaction that increases the disorder of the surroundings

So, product favoured reactions will prefer to have... ΔH ΔS

Thermodynamics

So, product favoured reactions will prefer to have... ΔH ΔS

This is quantitated by Gibbs Free energy - ΔG $\Delta G = \Delta H - T\Delta S$

Product-favoured reactions will have... ΔG

ΔS	ΔH	ΔG
+	−	
−	+	
+	+	
−	−	

$T\Delta S > \Delta H$

$\Delta H < T\Delta S$

- Chemical reactions will tend to be product favoured when...

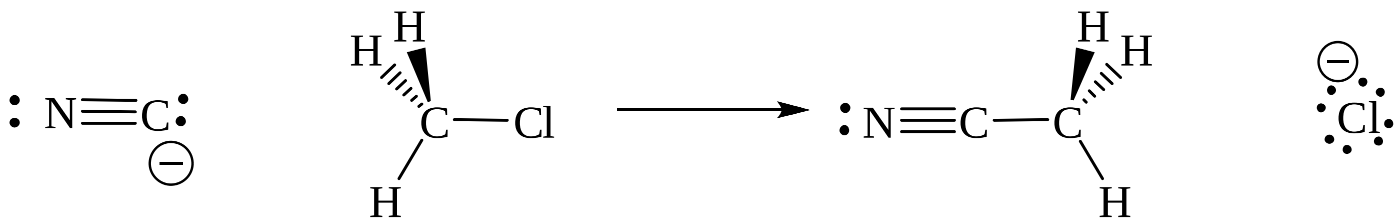
The bonds are stronger in the products than in the reactants ΔH

and

There are more product molecules than reactant molecules. ΔS

Chemical Reactions and Reaction Mechanisms

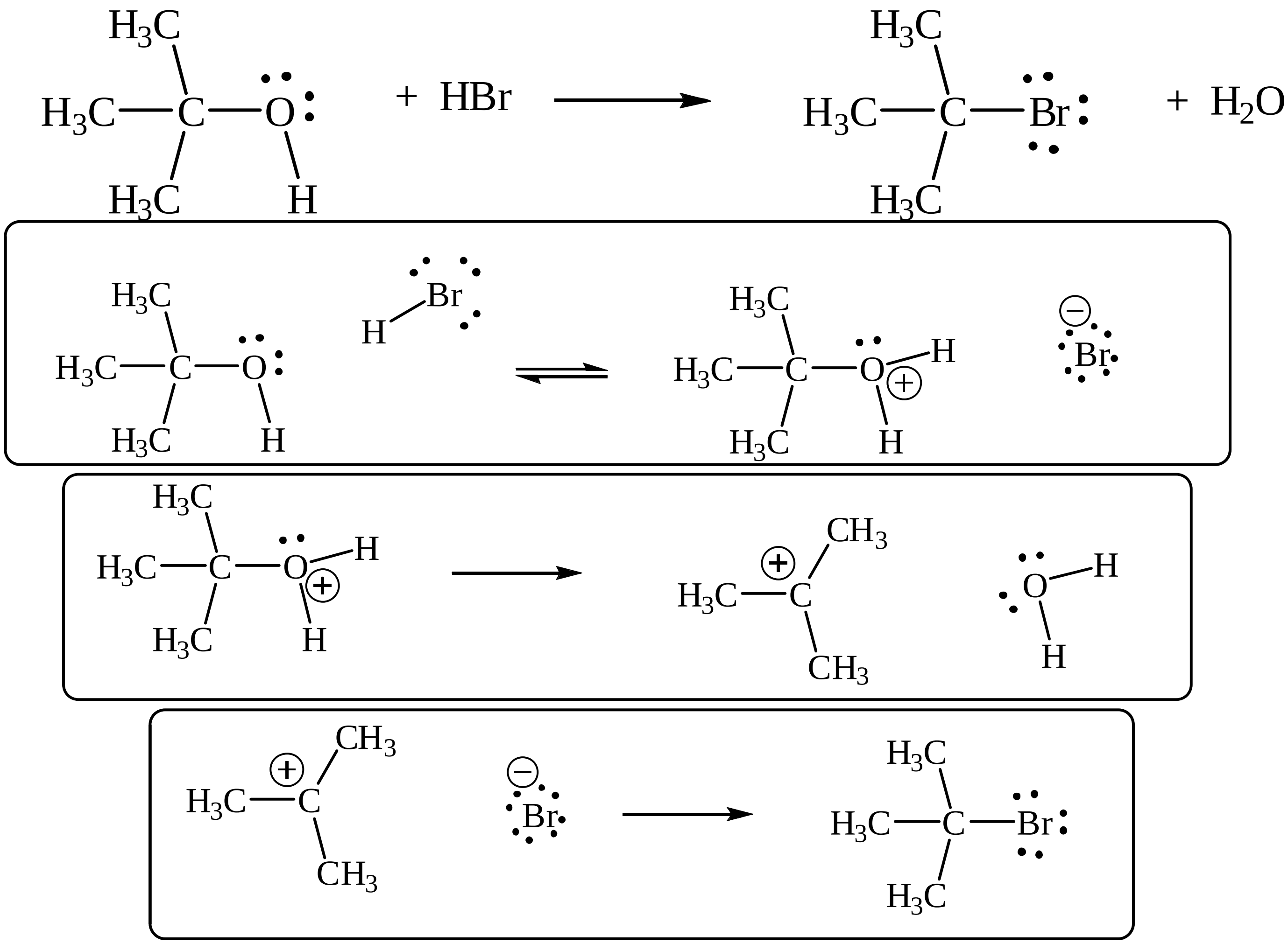
A reaction Mechanism describes the series of steps that the reactants take to form the products.



Each step in a reaction mechanism is referred to as an elementary process.

Chemical Reactions and Reaction Mechanisms

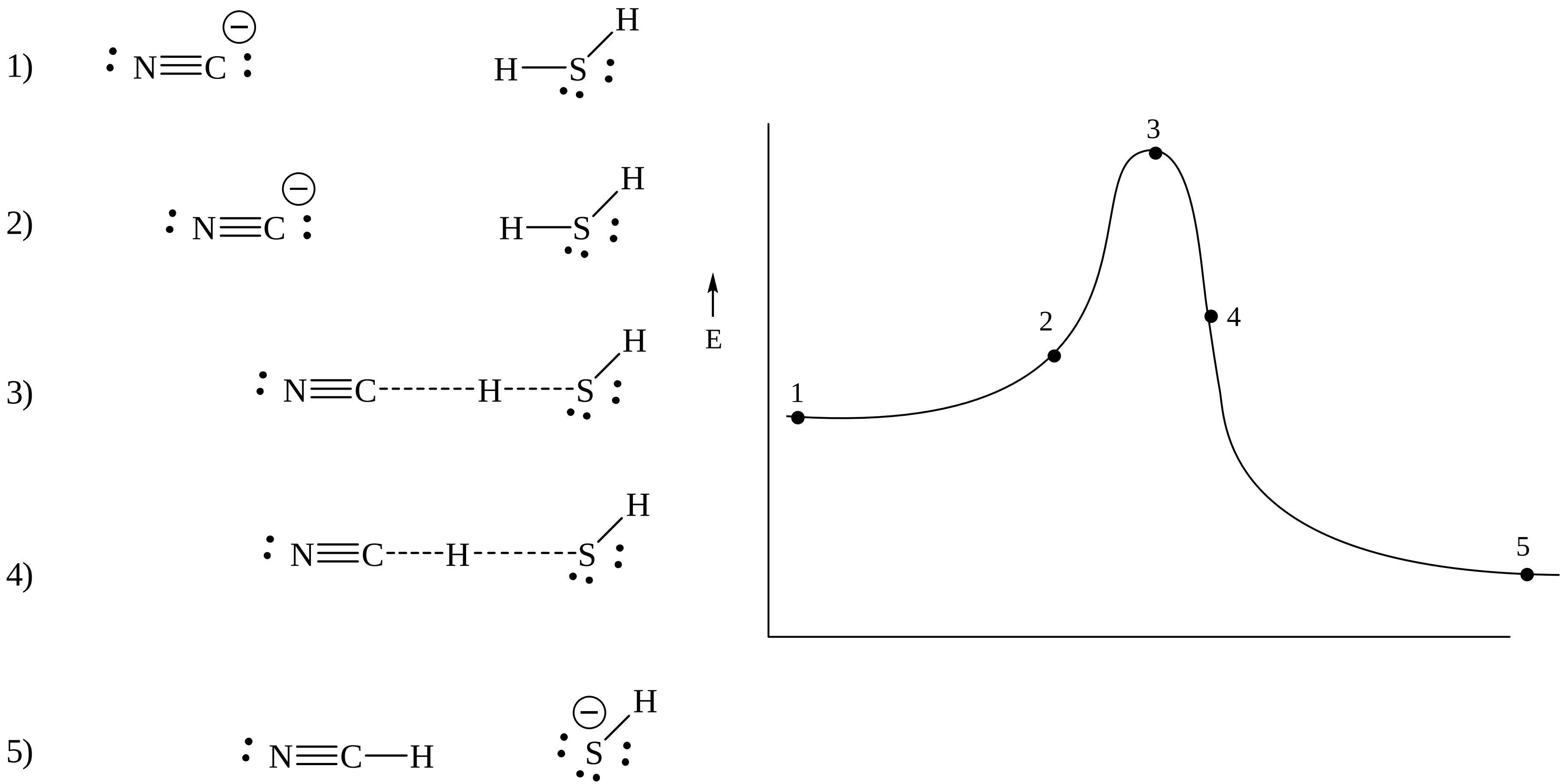
•The following reaction constitutes three elementary processes:



•Reactions consist of one or more elementary processes. The overall reaction is the sum of the elementary processes and the collection of these elementary processes describe the *reaction mechanism*.

Chemical Reactions and Reaction Mechanisms

•We can use a reaction profile diagram to follow the change in energy during an elementary process.

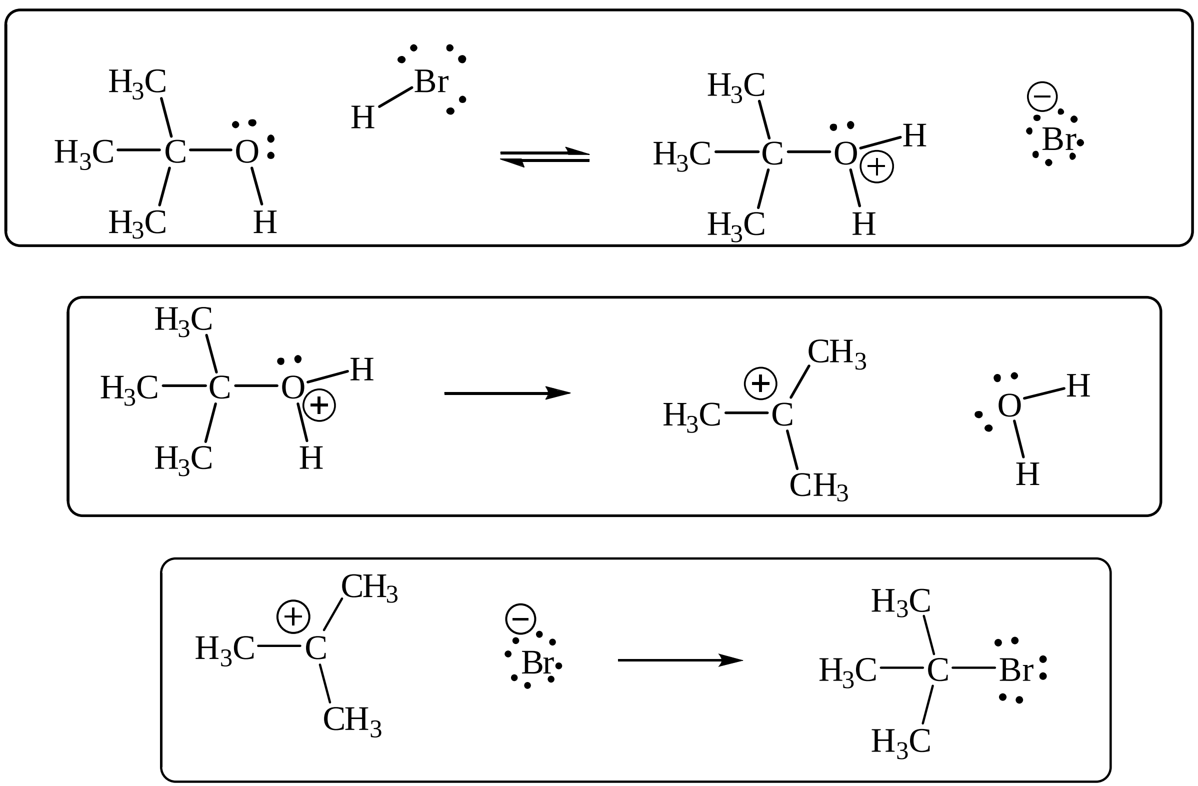


•The highest energy point on the reaction profile diagram occurs at the transition state for the reaction. A transition state is highly unstable and short lived and cannot be isolated or observed.

Chemical Reactions and Reaction Mechanisms

•Each elementary process will have its own transition state but it is NOT shown in the reaction mechanism.

•In multi step mechanisms (i.e. more than one elementary process) there will be intermediates, the products of elementary processes. Intermediates are semi stable molecules or ions that can often be observed. For a spontaneous reaction, intermediates will never be more stable than the final product.

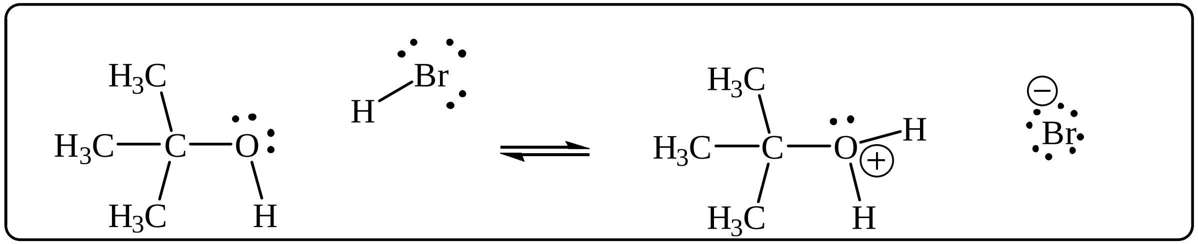


Chemical Reactions and Reaction Mechanisms

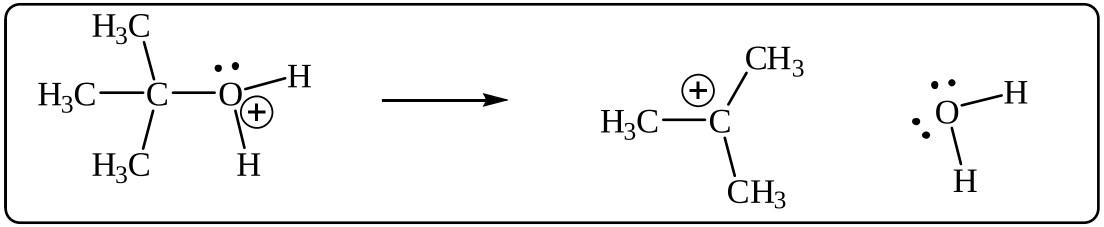
•A catalyst is a species that increases the rate of reaction by providing an alternative mechanism. Catalysts are neither created nor consumed.

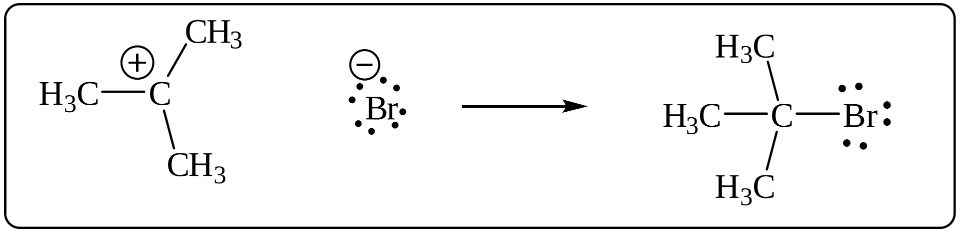
•In order to speed up the rate of reaction, a catalyst must speed up the rate determining step of the reaction. The rate determining step is the *slowest elementary process*.

•The rate determining step is the only step which affects the overall rate of the reaction – it is the 'bottleneck' of the reaction mechanism.



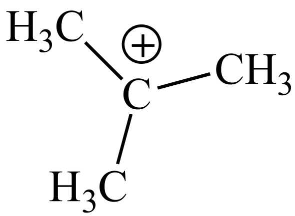
Which is the RDS?

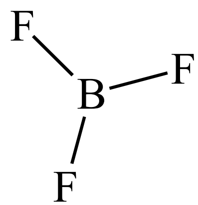


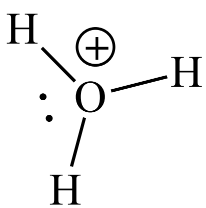


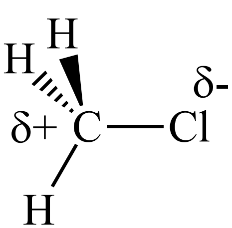
Operational Species

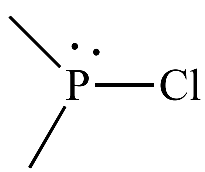
Electrophiles

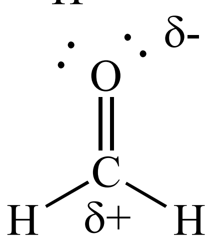




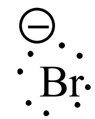


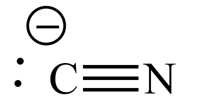


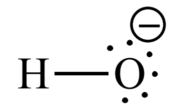


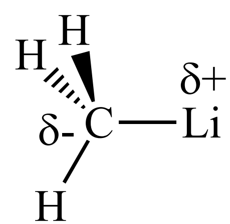


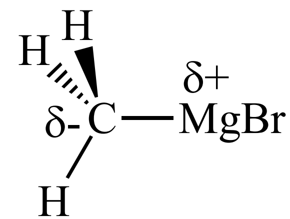
Nucleophiles

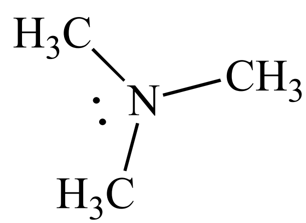


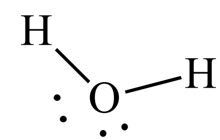


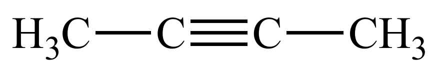


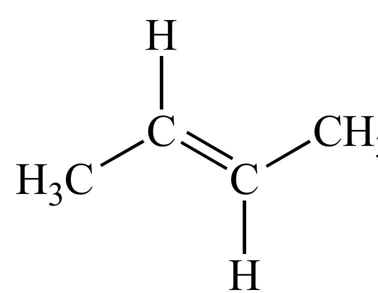










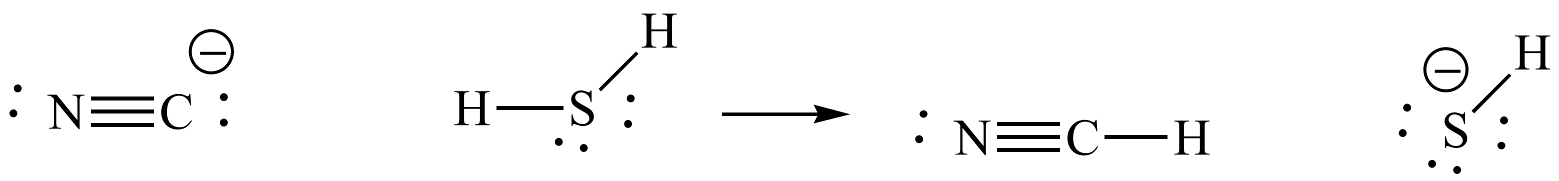


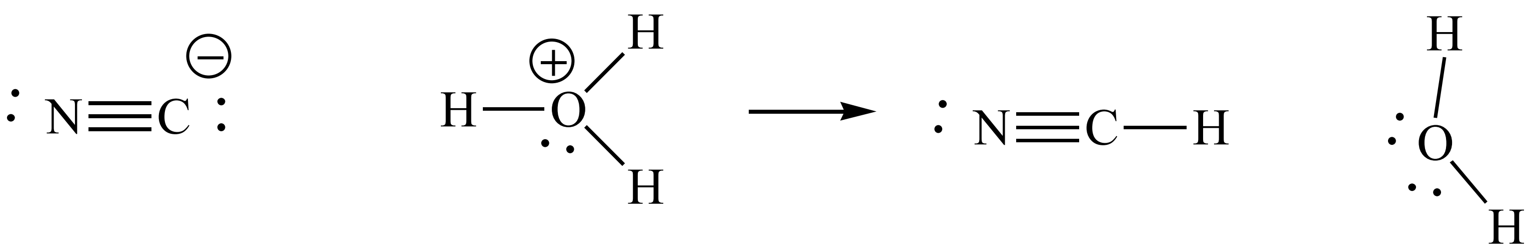
Operational Species

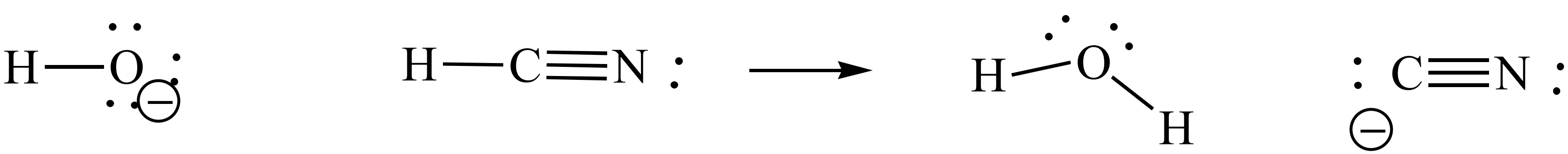
Common leaving groups:

Generic Molecule	Leaving Group	Conjugate Acid	pK_a of Conjugate Acid
R-I	I^-	HI	-11
R-Br	Br^-	HBr	-9
R-Cl	Cl^-	HCl	-7
R-OTs	TsO^-	HOTs	-6
$R\text{-}OH_2^+$	H_2O	H_3O^+	-1

Acids & Bases







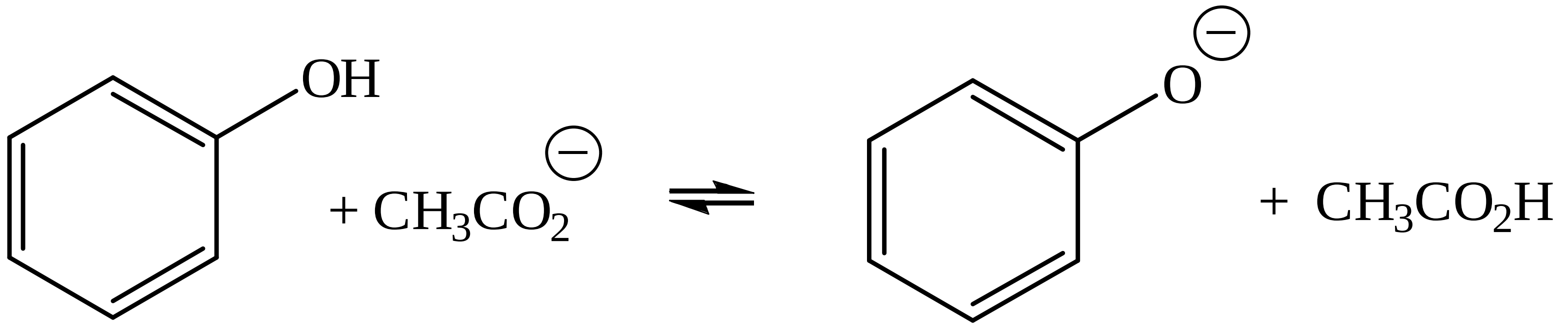
Acids & Bases

Some typical pKas.

Acid	Ka	pKa
$HClO_4$	10^{10}	-10
HF	7.2×10^{-4}	3.1
NH_4^+	6.3×10^{-10}	9.2
H_2O	2.0×10^{-16}	15.7
H_2	10^{-35}	35

Acids & Bases

•What does this mean for 'real life chemistry'?



K_a	1.0×10^{-10}	1.8×10^{-5}
pK_a	10	4.72

Keq =

•If you wanted this equilibrium to be product favoured, you would use a base…whose conjugate acid was weaker than phenol.

Acids & Bases

Table 5.1
(page 144)

pKa	Compound types
-10	mineral acids: H_2SO_4, HI, HBr, HCl, sulfonic acids RSO_3H
0	H_3O^+, H_3PO_4
5	Carboxylic acids, HF, thiophenols ArSH, HN_3
10	Weak inorganic acids (H_2S, HCN, NH_4^+, amine salts RNH_3^+, phenols ArOH, thiols (RSH), aromatic amides $ArCONH_2$
15	H_2O, alcohols ROH, amids $RCONH_2$)
20	Ketones (the alpha proton $H\text{-}CH_2COR$)
25	Esters (the alpha proton $H\text{-}CH_2CO_2R$), alkynes RCCH, nitriles ($H\text{-}CH_2CN$)
30	Anilines $ArNH_2$
40	Ammonia NH_3, amines RNH_2, benzylic protons $ArCH_3$
45	Arenes ArH and alkenes $RCH{=}CH_2$
50	Alkanes

Acids & Bases

Trends in Acidity

Across the period...

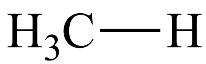
Acid	Conjugate Base	pKa
$H_3C—H$		45
$H_2N—H$		36
$HO—H$		15.7
$F—H$		3.1

Down a group...

$HO—H$		15.7
$HS—H$		11

Acids & Bases

Hybridization



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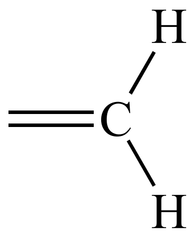

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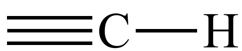

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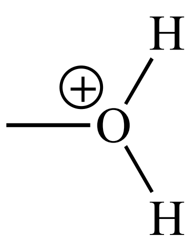
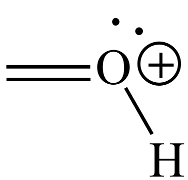


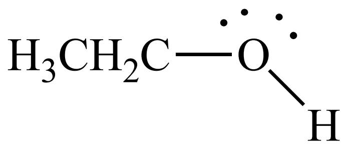
-2

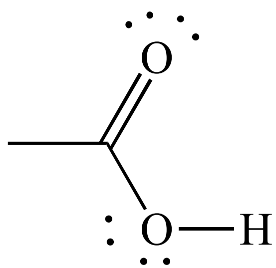


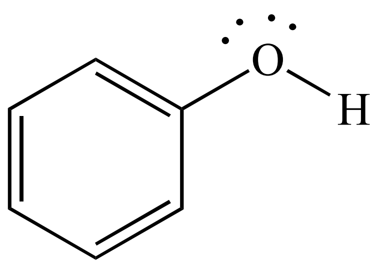
-4 to -10

Acids & Bases

pK_a **Resonance...**

17 

5 

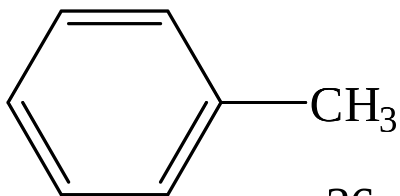
10 

Acids & Bases

Resonance effects greatly enhance the acidity of "activated" C—H bonds...

CH_4

45



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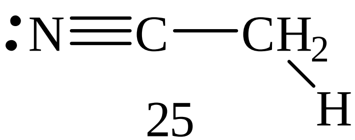

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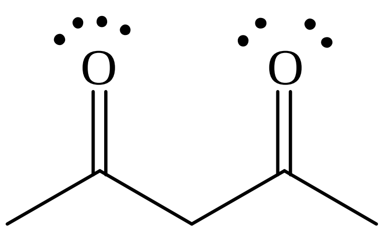

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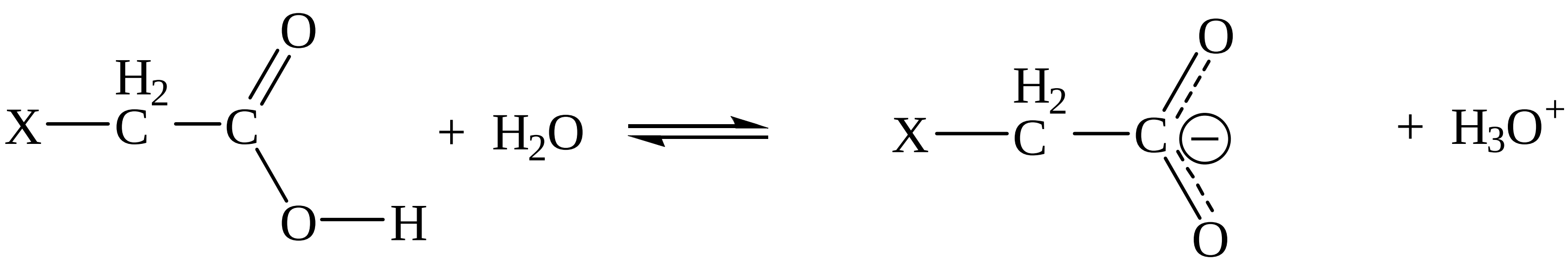
Acids & Bases

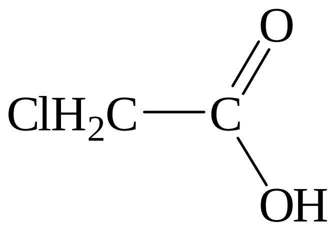
Inductive and Field effects



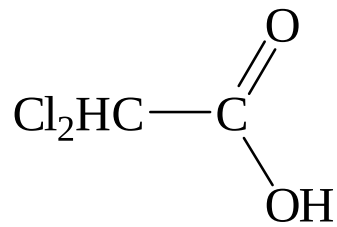
X	pKa
CH_3	4.87
H	4.76
I	3.17
Br	2.90
Cl	2.86
F	2.59
CN	2.46
NO_2	1.68

Acids & Bases

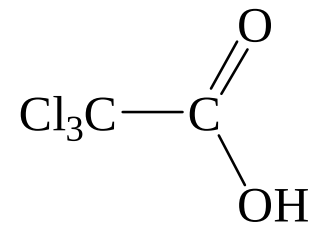
•These effects are…additive:



2.85

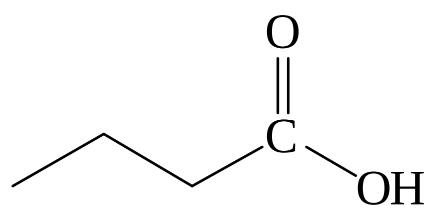


1.48

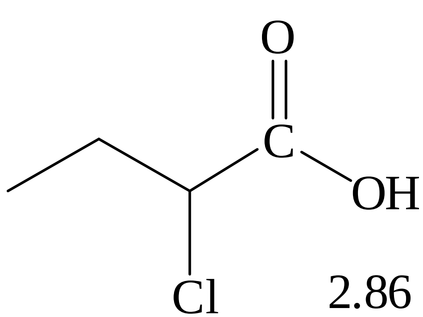


0.70

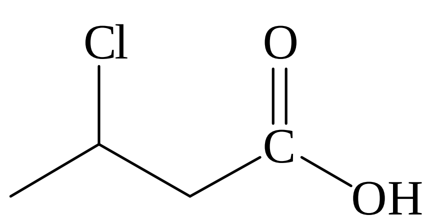
•These effects…drop off rapidly with increasing number of bonds:



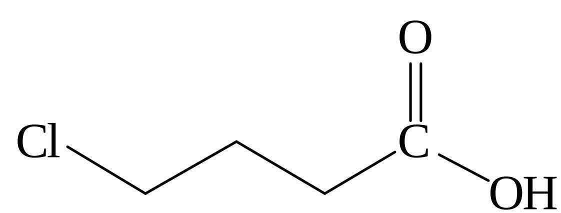
4.82



2.86



4.05



4.52