Part 2: Chapter 5 Summary

The idea of computing a mechanism

1) write down all possible reactions
2) Use rules to make sure no important reactions are missing.
    - must have initiation
    - must have catalytic cycle
    - should have termination
3) Use rules to eliminate excess reactions.
    - Ignore identity reactions
    - Ignore reactions with high barriers

$$E_a = E_a^0 + \gamma_P \Delta H_r$$

Table 5.4 Intrinsic barriers and transfer.
Coefficients for different types of reaction of neutral species.

Reaction	Example	Actual E_A^O kcal/mole	E_A^O to assume when predicting mechanisms kcal/mole	Actual γ_P	γ_P to assume when predicting mechanisms
Simple bond scission	$AB+X \rightarrow A+B+X$ X=a collision partner	0-1	1	1.0	1.0
Recombination	$A+B+X \rightarrow AB+X$ X=a collision partner	0-1	1	0.0	1.0
Exothermic atom transfer reaction	$R\text{x} + R^1 \rightarrow R + \text{x-}R^1$ x = an atom	8-16	12	0.2 to 0.6	0.3
Endothermic atom transfer reaction	$R\text{- x} + R \rightarrow R + \text{x-}R^1$ x=an atom	8-16	12	0.4 to 0.8	0.7
Ligand transfer reaction to hydrogen	$\text{H}+R\text{-}R^1 \rightarrow \text{H}R + R^1$	40-50	45	0.4 to 0.6	0.5
Other ligand transfer reactions	$\text{x} + R\text{-}R^1 \rightarrow \text{x}R + R^1$ x=an atom	50 or more	50	0.3 to 0.7	0.5

When does procedure fail?

- No initiation propagation reaction
- High Barriers to key steps
- Reactions occuring with a single concerted process

Reaction usually slow

Reactions with no initiation -propagation reaction

$$2Na + Cl_2 \Rightarrow 2NaCl$$

(5.82)

$$Na + Cl_2 \rightarrow NaCl + Cl$$

(5.88)

now what?

$$Na + Cl \xrightarrow{wall} NaCl$$

(5.89)

$$Na + Cl + X \rightarrow NaCl + X$$

Low rate (requires 3 body collision)

Reactions with high barriers

$$2CH_4 \Rightarrow C_2H_6 + H_2$$

(5.93)

$$CH_4 \rightarrow CH_3 + H$$

(5.94)

$$H + CH_4 \rightarrow CH_3 + H_2$$

(5.95)

$$CH_3 + CH_4 \rightarrow C_2H_6 + H$$

(5.96) (high intrinsic barrier)

$$H_f(CH_3CH_3) = -20$$

$$H_f(H) = +52.1$$

$$H_f(CH_4) = -17.9$$

$$H_f(CH_3) = +34.8$$

$$\Delta H_r = -20 + 52 - (-17.9) - 34.8 = +15.5$$

$$E_A^{\circ} = 45 \text{ (Hydrogen is product)}$$

$$E_A = 45 + 0.5 x 15.5 = 52.9 \text{kcal/mole}$$

$$H + CH_3 \rightarrow CH_4$$

(5.97)

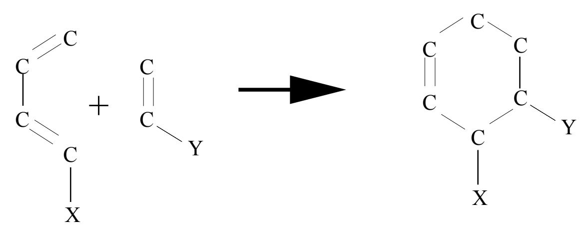
Very slow reactions: Usually not seen!!

Requires temp of 52.5/0.07 = 750K

Association reactions

$$NH_3 + HCl \Rightarrow NH_4Cl$$
(5.90)

$$NH_3 + HCl + X \rightarrow NH_4Cl + X$$
(5.91)



(5.92)

Unimolecular reactions

$$\text{Cyclopropane} \Rightarrow \text{Propene}$$

(5.100)

$$CH_3NC \Rightarrow CH_3CN$$

(5.101)

Could 5.101 go by an initiation/propagation mechanism?

$$CH_3NC \rightarrow CH_3 + NC$$

(5.102)

$$CH_3NC + CH_3 \rightarrow CH_3 + NCCH_3$$

(5.103)

$$CH_3 + NC \rightarrow CH_3CN$$

(5.104)

Lindemann mechanism

$$\text{Methyl isocyanide} + X \rightarrow \text{excited methyl-isocyanide} + X$$
$$\text{excited isocyanide} \rightarrow \text{methylcyanide}$$

(5.105)

Concerted Eliminations

$$X + CH_3CH_2CH_2CH_3 \rightarrow 2CH_3CH_2 + X$$
(5.106)

$$X + C_4H_{10} \rightarrow CH_3CHCHCH_3 + H_2 + X$$
(5.107)

Summary of general rules for radical reactions

Table 5.5 Summary of the Initiation-Propagation mechanisms of radicals.
1) Initiation Step - Weakest bond in reactants break to yield radicals 2) Radical reacts via a catalytic cycle - Atoms transferred one atom at a time - Must be cycle 3) Termination Step - Radicals recombine
Exceptions: No catalytic cycle where atoms are transferred one atom at a time.

New Topic: Reactions of Ions

Table 5.6 Some examples of Ion Reactions.		
Reaction	Simplified Mechanism	Typical Application
Isomerization $CH_3CH_2CH=H_2 \overset{H^+}{\Rightarrow}$ $CH_3CH=CHCH_3$	$CH_3CH_2CH{=}CH_2{+}\overset{+}{H}\rightarrow$ $\left[CH_3CH_2CH^+{-}\overset{H}{C}H_3\right]^+$ $CH_3CHC{=}CHCH_3{+}H^+$	Octane Enhancement Monomer Production
Cracking $C_{10}H_{20} \overset{H^+}{\Rightarrow} 2C_5H_{10}$	$C_{10}H_{20}{+}H^+\rightarrow$ $\left[C_{10}H_{21}\right]^+\rightarrow$ $C_5H_{10}{+}C_5H_{11}{}^+$ $C_5H_{11}{}^+\rightarrow C_5H_{10}{+}H^+$	Crude Oil Conversion Biological Conversions
Alkylation $CH_3OH + C_6H_6 \overset{H^+}{\Rightarrow}$ $CH_3C_6H_5 + H_2O$	$CH_3OH{+}H^+\rightarrow$ $CH_3^+{+}H_2O$ $CH_3^+{+}C_6H_6\rightarrow CH_3C_6H_6{}^+$ $CH_3C_6H_6\rightarrow CH_3C_6H_5{+}H^+$	Pharmaceutical Production Monomer Production Fine Chemicals
Esterfication $CH_3COOH + CH_3OH \overset{H^+}{\Rightarrow}$ $CH_3COOCH_3 + H_2O$	$CH_3COOH\rightarrow CH_3COO^-{+}H^+$ $CH_3OH{+}H^+\rightarrow CH_3^+{+}H_2O$ $CH_3^+{+}CH_3COO^-\rightarrow CH_3COOCH_3$	Soap Production Fragrance Production

Ions have lower pauli repulsions: leads to additional reactivity

Example:

$$CH_3CH_2OH \overset{H^+}{\Rightarrow} H_2C = CH_2 + H_2O$$
(5.109)

goes by the following mechanism in the presence of HCl. First, the acid dissociates yielding protons (i.e., H^+) and chloride ions:

$$HCl \xrightarrow{e^-} H^+ + Cl^-$$
(5.110)

Then the protons react with the ethanol to yield a charged complex:

$$H^+ + C_2H_5OH \rightarrow [C_2H_5OH_2]^+$$
(5.111)

Then the charged complex decomposes yielding a water and an ethyl carbonium ion:

$$[C_2H_5OH_2]^+ \rightarrow [C_2H_5]^+ + H_2O$$
(5.112)

Then the ethyl carbonium ion decomposes yielding ethylene and the proton:

$$[C_2H_5]^+ \rightarrow C_2H_4 + H^+$$
(5.113)

Finally the proton can recombine with chlorine:

$$H^+ + Cl^- \rightarrow HCl$$
(5.114)

There is one subtle point: it is hard to form ions in the gas phase. One often uses electrons to produce ions. So, for example, one could replace reaction (5.110) by:

$$H_2 + e^- \rightarrow H^+ + H + 2e^-$$

(5.115)

Ions have unusual bonding: changes reactivity

$$D + CH_3CH_3 \rightarrow H + DCH_2CH_3$$
(5.116)

and a dehydrogenation:

$$D + CH_3CH_3 \rightarrow DH + CH_2CH_3$$
(5.117)

In principle, one might also see bond scission:

$$D + CH_3CH_3 \rightarrow DCH_3 + CH_3$$
(5.118)

However, reaction (5.118) has never been observed experimentally.

If one instead runs reaction with D^+, the main reactions are:

$$\mathrm{D}^{+} + \mathrm{CH_3CH_3} \rightarrow \left[\mathrm{H_3C'} \overset{\mathrm{D}}{\text{—}} \mathrm{'CH_3} \right]^{+}$$

(5.119)

$$\left[\mathrm{H_3C'} \overset{\mathrm{D}}{\text{—}} \mathrm{'CH_3} \right]^{+} \rightarrow \mathrm{DCH_3} + \mathrm{CH_3}^{+}$$

(5.120)

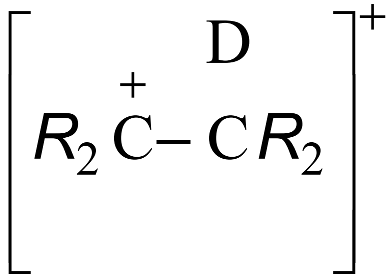
$$\mathrm{D}^{+} + R_2\mathrm{C} = \mathrm{C}R_2 \rightarrow \left[R_2\mathrm{C'} \overset{\mathrm{D}}{\text{—}} \mathrm{'C}R_2 \right]^{+}$$

(5.121)

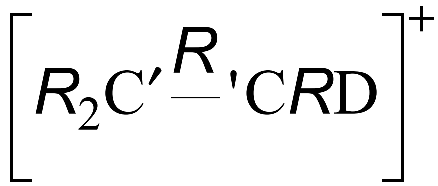
i.e.:

$$\left[R_2\mathrm{C'} \overset{\mathrm{D}}{\text{—}} \mathrm{'C}R_2 \right]^{+}$$

(5.122)



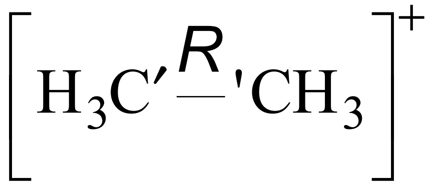
(5.123)



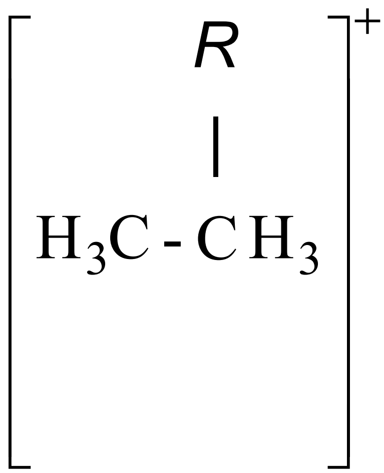
(5.124)

Mechanism of ion reactions:

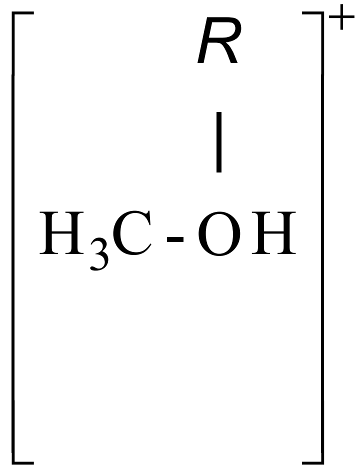
Carbonium ions:



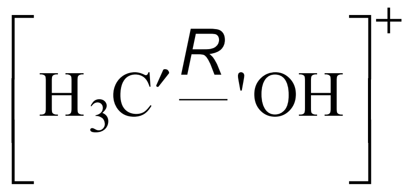
(5.125)



(5.126)



(5.127)



(5.128)

carbenium ions

$$H_3C^+$$

(5.129)

$$RH_2C^+$$

(5.130)

$$R_2HC^+$$

(5.131)

$$R_3C^+$$

(5.132)

$$\left[R_2C' \overset{\mathrm{H}}{\text{—}} 'CH_2 \right]^+$$

(5.133)

Carbonium ions: Cracking and isomerization:

$$\mathrm{H} + R\mathrm{CH_2} - \mathrm{CH_2}R \rightarrow \left[R\mathrm{H_2C}' \overset{\mathrm{H}}{—} {}^{`}\mathrm{CH_2}R \right]^+$$

(5.134)

Cracking

$$\left[R\mathrm{H_2C}' \overset{\mathrm{H}}{—} {}^{`}\mathrm{CH_2}R \right]^+ \rightarrow R\mathrm{CH_3} + \mathrm{CH_2}R^+$$

(5.135)

Isomerization:

$$\left[\mathrm{H_3}\,\overset{R}{\overset{/}{\mathrm{C}}} - \mathrm{CH_3} \right]^+ \rightarrow \left[\mathrm{H_3C}' \overset{R}{—} {}^{`}\mathrm{CH_3} \right]^+ \rightarrow \left[\mathrm{H_3C} - \overset{R}{\overset{/}{\mathrm{C}}}\,\mathrm{H_3} \right]^+$$

(5.136)

Carbenium ions can also crack and isomerize.
β-scission

$$
\begin{array}{ccccccccccccccccccccc}
 & & \mathrm{H} & & \mathrm{H} & & R & & + & & & & & \mathrm{H} & & \mathrm{H} & & & R & & \mathrm{H} \\
R' & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} & \rightarrow & R' - & \mathrm{C} & - & \mathrm{C}+ & & + & \mathrm{C} & = & \mathrm{C} \\
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & & \mathrm{H} & & \mathrm{H} & & & \mathrm{H} & & \mathrm{H}
\end{array}
$$

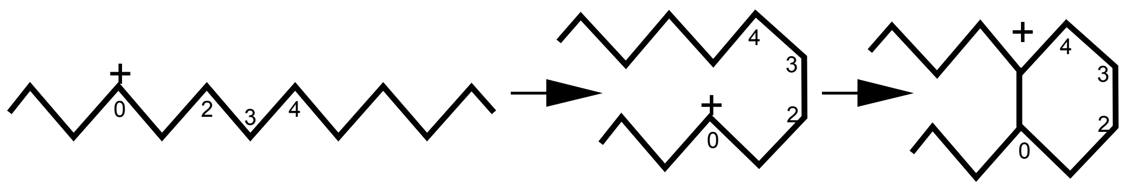
(5.137)

Isomerization: 1, 2 shift

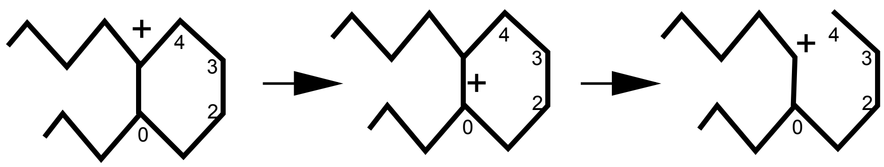
$$
\begin{array}{cccccccccccccccccccc}
 & & \mathrm{H} & & \mathrm{H} & & R & & + & & & & & \mathrm{H} & & \mathrm{H} & & + & & R \\
R' & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & R'' & \rightarrow & R' - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} - R'' \\
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H}
\end{array}
$$

(5.138)

6-centered isomerization



(5.139)



(5.140)

Alkylation:

$$B^{+} + R_3C - CR_2H \rightarrow \left[R_3C' \overset{B}{—} {}' CR_2H \right]^{+}$$

(5.141)

$$\left[R_3C' \overset{B}{—} CR_2H \right]^{+} \rightarrow R_3C - CR_2B + H^{+}$$

(5.142)

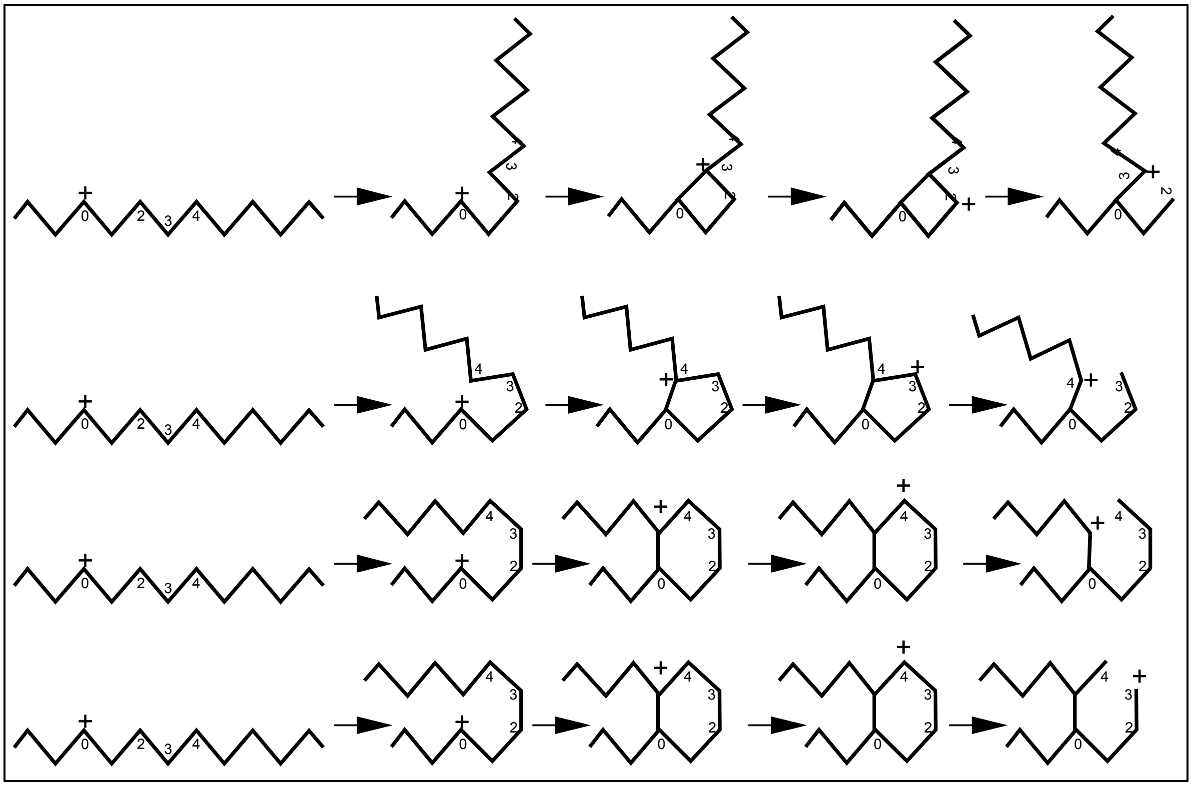


Figure 5.7 Some of the reactions of a tridecyl-cation, adapted from Martens and Jacobs[1990].

Table 5.7 The products of tridecyl-cation ($C_{13}H_{25}^{+}$) isomerization in different environments. Results of Martens and Jacobs[1990]

Species	Production in the Gas Phase	Production in Platinum/CAY zeolite catalyst	Production in Platinum/USY zeolite catalyst
2 methyl-dodecane	9.3	7.0	11
3-methyl-dodecane	17.7	15.1	17.9
4-methyl-dodecane	19.0	18.4	18.0
5-methyl-dodecane	19.1	22.8	19.6
6-methyl-dodecane	19.1	23.4	19.4
3 ethyl-undecane	2.7	1.9	2.7
4 ethyl-undecane	3.4	3.4	3.4
5 ethyl-undecane	3.9	3.6	3.9
6-ethyl-undecane	2.2	2.0	2.2
4-propyl-decane	1.0	0.7	1.0
5-propyl-decane	1.8	1.4	1.8
5-propyl-decane	0.7	0.3	0.7

Mechanisms of ionic reactions

Initiation: produce ions
propagation cyclic pathways
termination lose ions.

Generally like highly coordinated centers
charge solvent confuses things

Only a few basic reactions
S_N1, S_N2, E_1, E_2, isomerizations.

My experience - ionic reactions messy - more possibilities, hard to predict intrinsic barriers

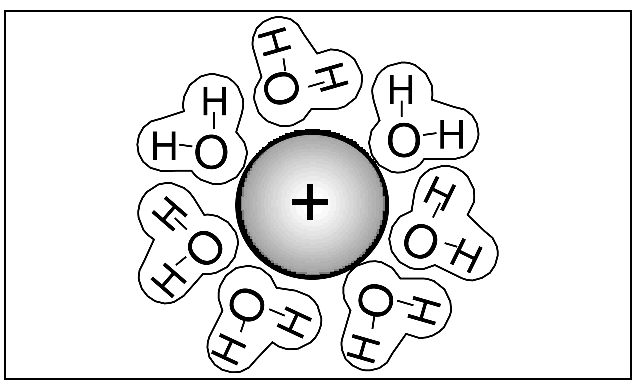


Figure 5.9 A schematic of the solvent cage around an ion in solution.

New Topic: Reactions on metal surfaces

Table 5.9 Some examples of reactions on metal surfaces	
Hydrogenation $N_2+3H_2 \rightarrow 2NH_3$ $C_2H_4+H_2 \rightarrow C_2H_6$	Chemical Production Crude Oil Upgrade Essential Oil Upgrade
Dehydrogenation $C_2H_4 \xrightarrow{Pt} C_2H_2 + H_2$	Octane Enhancement Monomer Production
Oxidation $2CO + CO \xrightarrow{Pt} 2CO_2 + N_2$ $C_2H_4 + 1/2O_2 \xrightarrow{Ag} C_2H_4O$ $2NH_3 + 4O_2 \xrightarrow{Pt} N_2O_5 + 3H_2O$	Catalytic converters Monomer Production Chemicals Production
Chemical Vapor Deposition $Al(C_2H_5)_3 \xrightarrow{Al} Al + 3C_2H_4 + 3/2H_2$	Connections on Integrated Circuits
$Fe_{(s)} \rightarrow Fe^{3+}_{(Aq)}$	Corrosion

Mechanism on surface similar to radical reactions in gas phase - but radicals bound to surface

$X + H_2 \rightarrow 2H + X$	$H_2 + 2S \rightarrow H_{(ad)}$
$X + O_2 \rightarrow 2O + X$	$O_2 + 2S \rightarrow 2O_{(ad)}$
$O + H_2 \rightarrow OH + H$	$O_{(ad)} + H_2 \rightarrow OH_{(ad)} + H_{(ad)}$
$H_2 + OH \rightarrow H_2O + H$	$2O_{(ad)} + H_2 \rightarrow 2OH_{(ad)}$
$H + O_2 \rightarrow OH + O$	$O_{(ad)} + H_{(ad)} \rightarrow OH_{(ad)}$
$X + 2H \rightarrow H_2 + X$	$2OH_{(ad)} \rightarrow H_2O + O_{(ad)}$
(5.152)	$H_{(ad)} + OH_{(ad)} \rightarrow H_2O$
	$H_2 + 2S \rightarrow 2H_{(ad)}$
	(5.153)

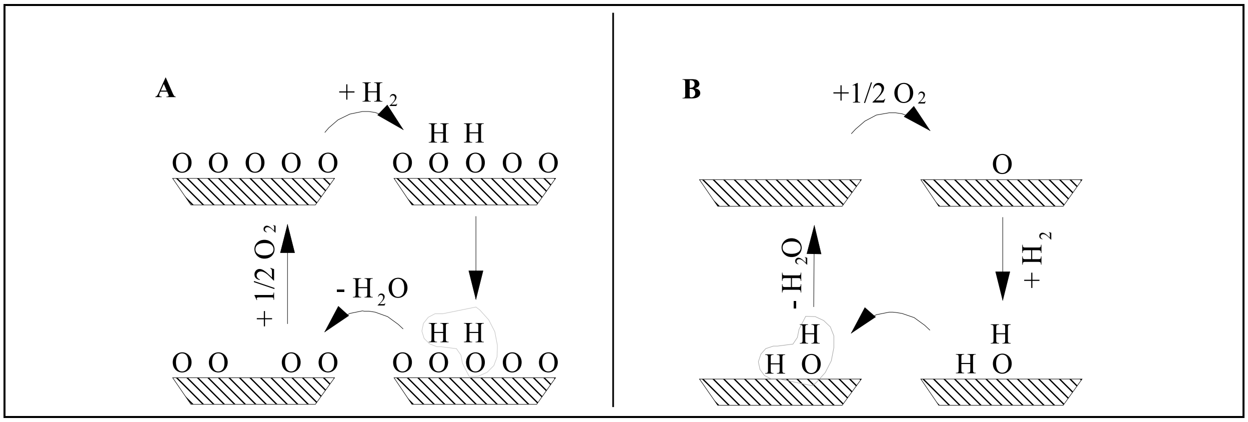


Figure 5.10 Catalytic cycles for the production of water a) via disproportion of OH groups, b) via the reaction $OH_{(ad)}+H_{)ad)}\rightarrow H_2O$.

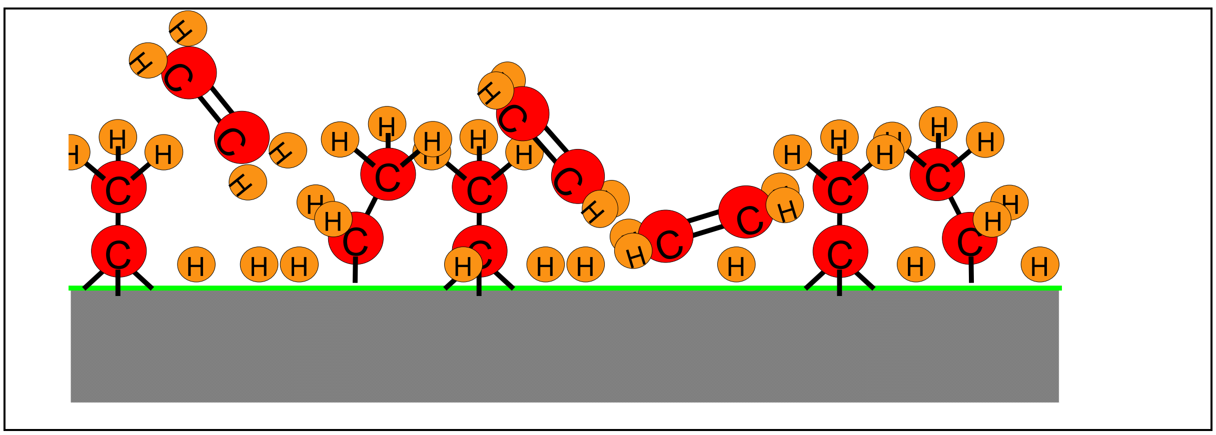


Figure 5.11 An illustration of the adsorbed phase when ethylene adsorbs on platinum.

key terms

- adsorption
- adsorbed
- adsorbate
- adsorbent

Molecular adsorption vs dissociative adsorption

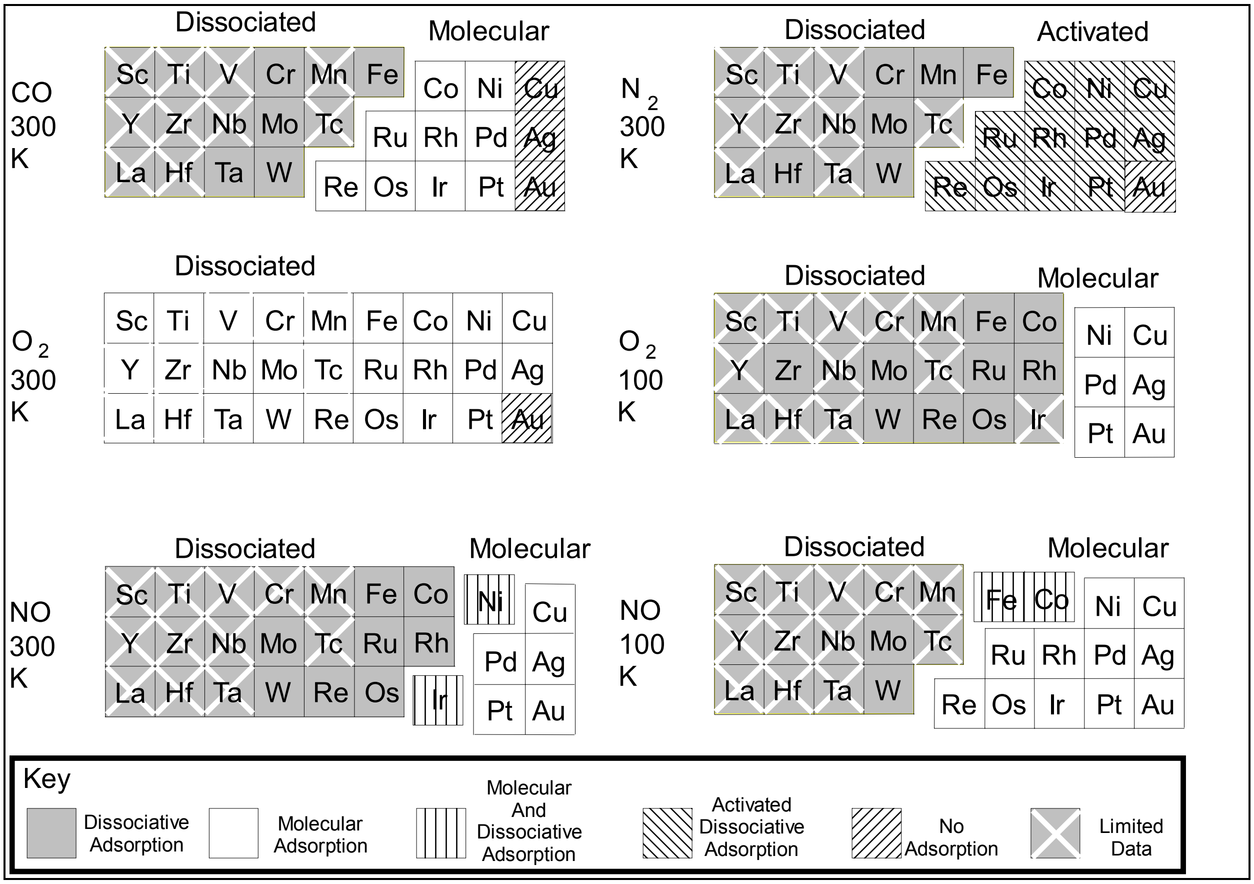


Figure 5.12 The metals which dissociate CO, NO, H_2, O_2 and CO at various temperatures.

Surface structure

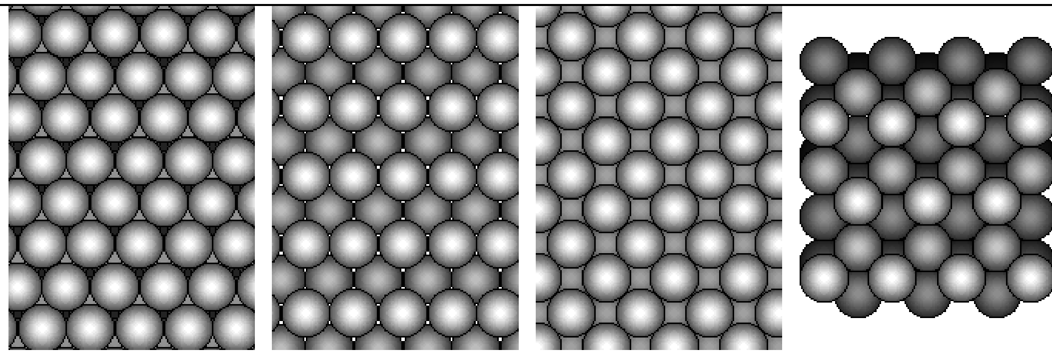


Figure 5.13 Pictures of Some Common Surface Structures.

Mechanisms of surface reactions: similar to gas phase reactions except initiation is formation of a bare surface site

All Surface Reactions Occur In Cycles Where Bare Surface Sites Are Formed And Destroyed

(5.154)

Example

$$CH_3OH \Rightarrow CO + 2H_2$$
(5.155)

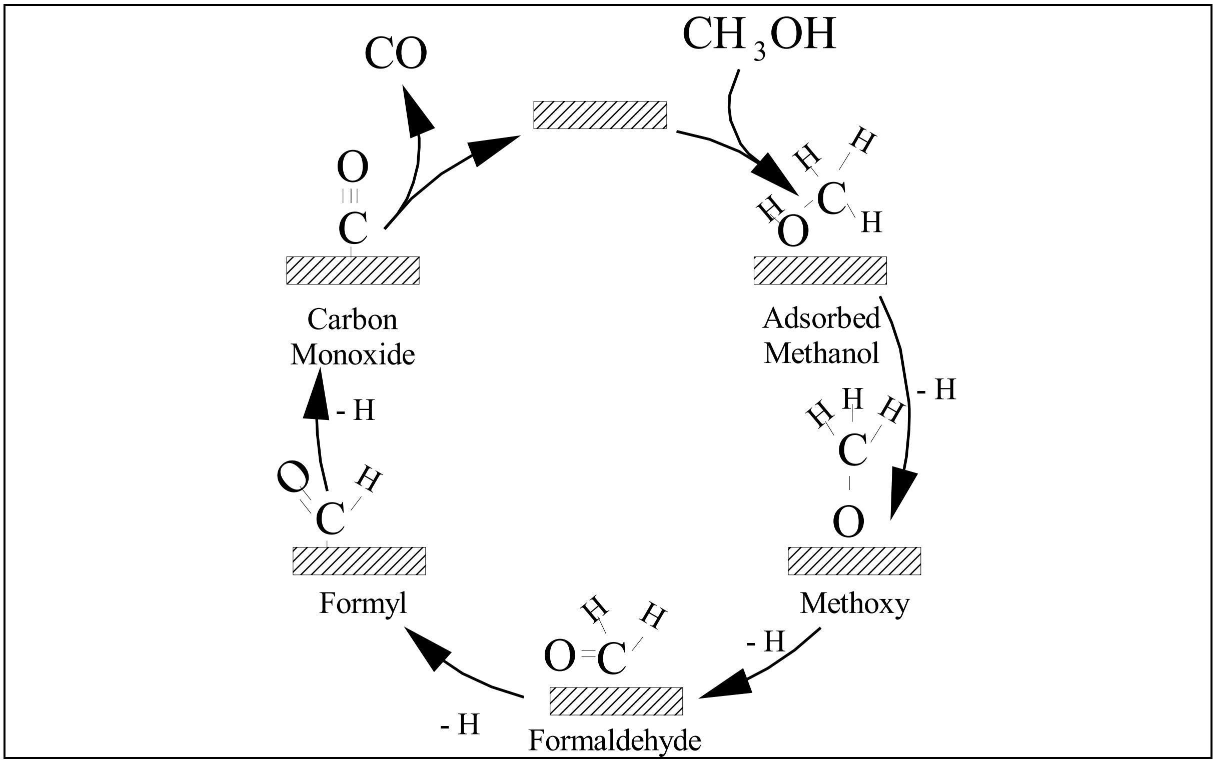


Figure 5.14 The Mechanism of Methanol Decomposition on Pt(111).

notation S=surface site

$$CH_3OH_{(ad)} + S \rightarrow CH_3O_{(ad)} + H_{(ad)}$$
(5.156)

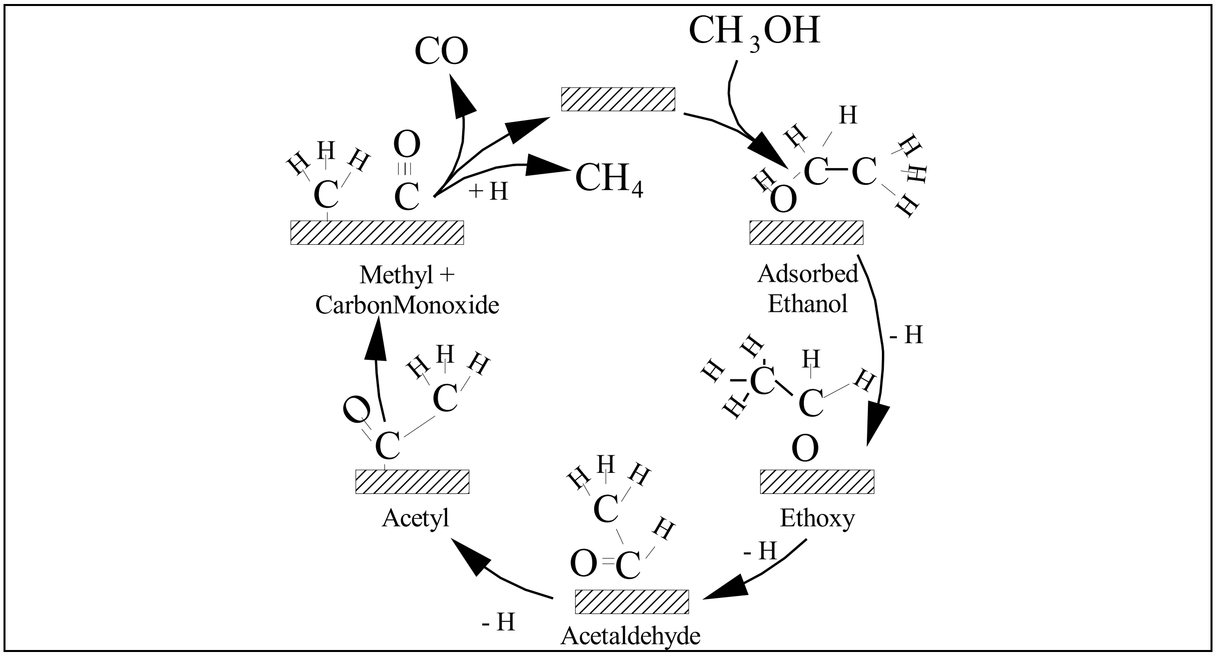


Figure 5.15 The Mechanism of Ethanol Decomposition on Pt(111).

Notice C-C bond breaks!

Rules to predict mechanisms

Polayni relationship + proximity effect

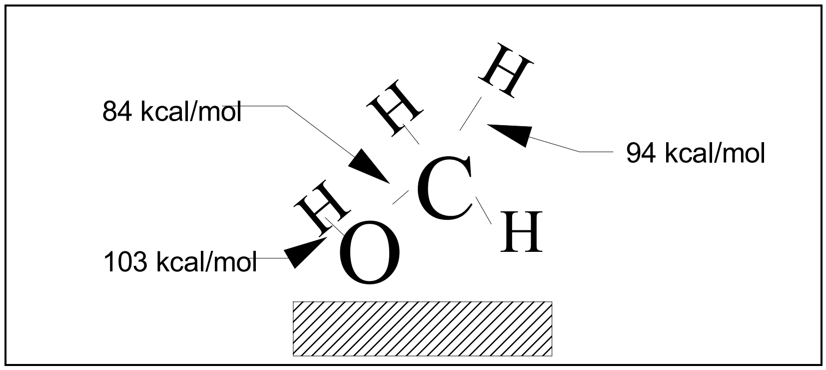


Figure 5.16 Bond Energies in Methanol

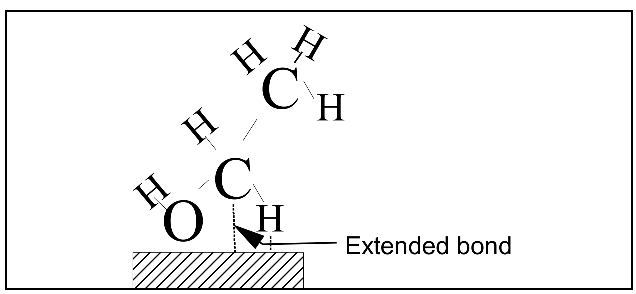


Figure 5.17 The transition state for C-H scission in adsorbed ethanol.

Example methanol decomposition

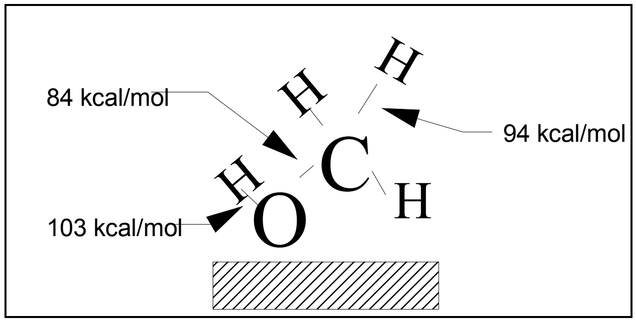


Figure 5.17 Bond energy in methanol.

OH breaks first proximity effect
CH next
Yields CO

Example ethanol

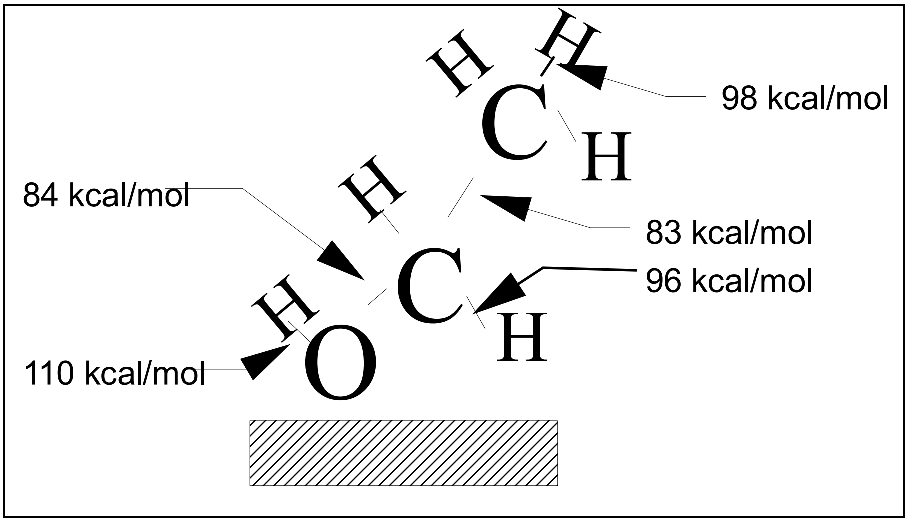


Figure 5.18 Bond energy in ethanol.

OH breaks first proximity effect
CH next

eventually get to $CH_2CO_{(ad)}$

here is where it gets tricky

C-C Bond in $CH_3CO_{(ad)}$ is only 55 kcal/mole compared to 100 kcal/mole for C-H bond. Enthalpy wins!!

Generic types of surface reactions

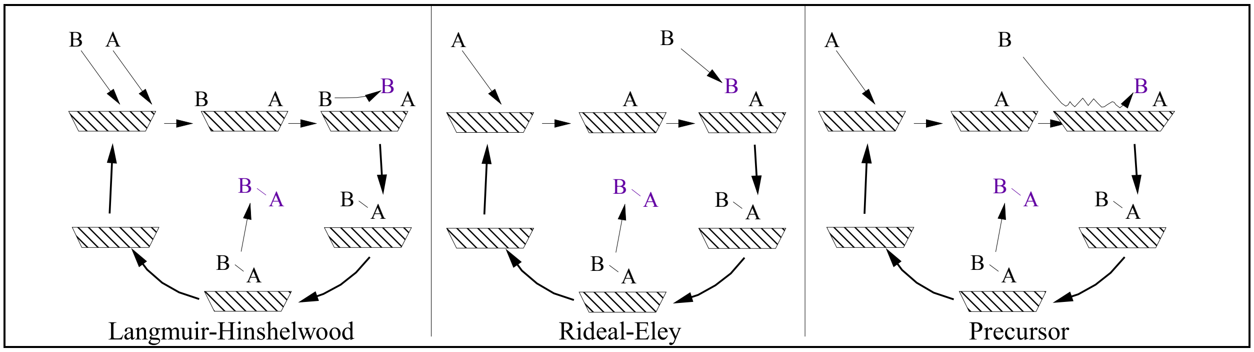


Figure 5.20 Schematic of a) Langmuir-Hinshelwood, b) Rideal-Eley, c) precursor mechanism for the reaction A+B⇒AB and AB⇒A+B.

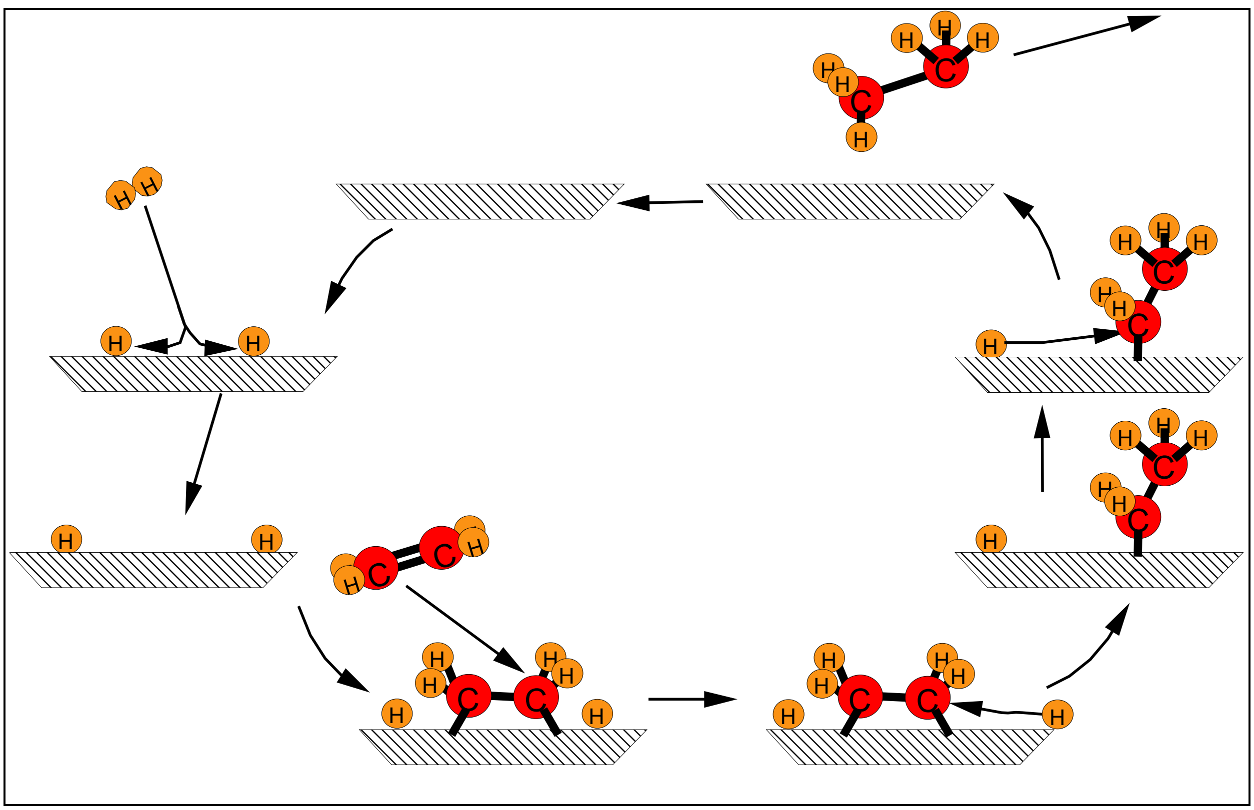


Figure 5.21 A Langmuir-Hinshelwood mechanism for the reaction $C_2H_4+H_2 \Rightarrow C_2H_6$.

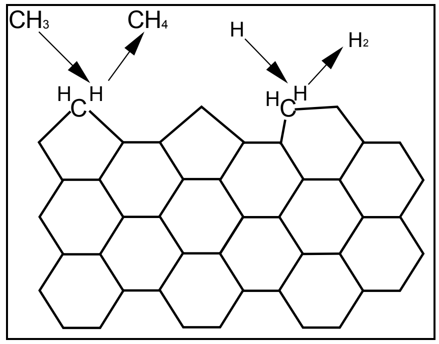


Figure5.22 A Rideal-Eley mechanism for diamond deposition.

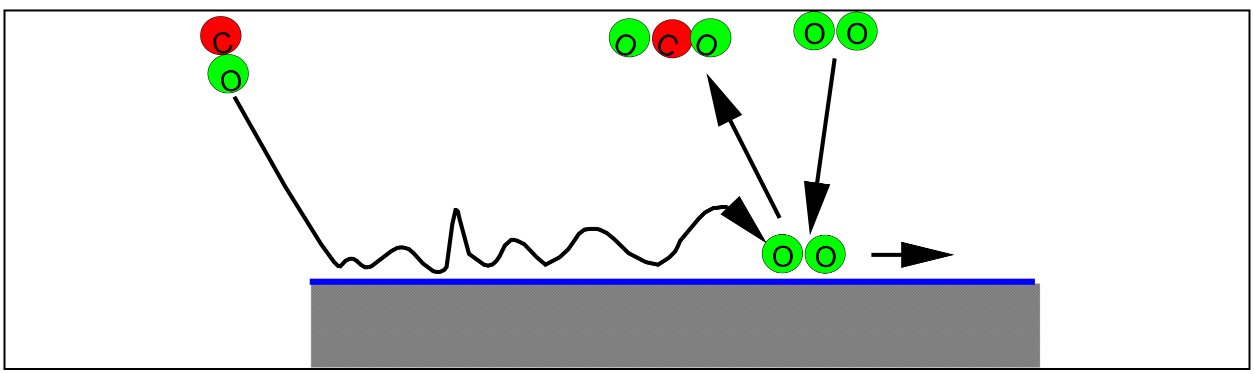


Figure 5.23 A precursor mechanism for the reaction $2CO+O_2 \Rightarrow CO_2$.

Summary of mechanism of reaction on metals

Mechanisms on metals similar to gas phase-

Key difference - species bound to surface

- proximity effect
- di-radicals, tri-radicals possible