Alkenes: Structure & Properties

Alkane (acyclic): C_nH_{2n+2} > saturated.

Alkene (acyclic): C_nH_{2n} > unsaturated.

eg ethylene (IUPAC: ethene), C_2H_4: $H_2C{=}CH_2$

The carbon-carbon double bond is the distinguishing feature of alkenes.

It is formed between two sp^2 carbons. One bond is σ, formed by head to head overlap of sp^2 orbitals; the second is π, formed by overlap of parallel 2p orbitals. The π bond has two halves, one above and the other below the plane defined by the two carbons and the four other atoms to which they are attached.

The bond angles around the sp^2 carbons are . 120^o.

σ-bond requires *ca.* 90 kcal/mole to break.

π-bond requires *ca*. 65 kcal/mole to break.

Owing to the shape of the π-bond and its strength, there is not free rotation around a double bond as there is around most single bonds.

The butenes: C_4H_8

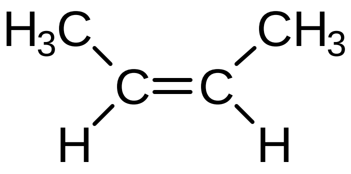
CH_3-CH_2-CH=CH_2 : 1-butene,

$(CH_3)_2C$=CH_2 : 2-methylpropene

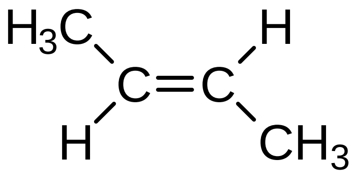
CH_3-CH=CH-CH_3 : 2-butene

Appear to be 3 isomers, but look again!

There are two isomeric 2-butenes, for 4 butene isomers in all.



cis-2-butene



trans-2-butene

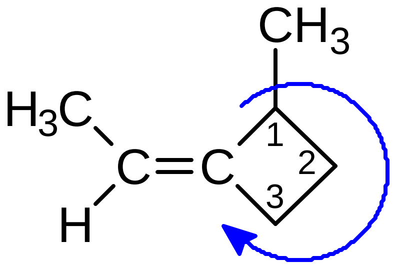
The cis/trans isomers are configurational (not conformational) stereoisomers and are sometimes called *geometric isomers.*

These isomers have different properties:
cis- bp = 4°C, mp = -139°C;
trans- bp = 1°C, mp = -106°C.

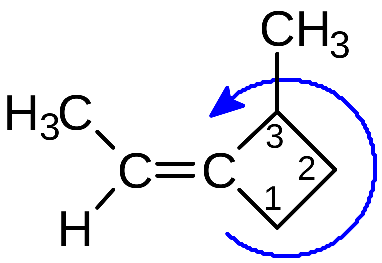
The potential for geometric isomerism will exist in alkenes unless at least one of the carbons joined by the double bond carries two identical groups.

If one of the carbons is part of a ring to which the double bond is exocyclic, the carbon is considered to carry two identical groups if, starting at the trigonal carbon, traversing the ring in the clockwise direction is the same as traversing it in a counterclockwise direction; otherwise this carbon is considered to carry two different groups.

In the case below, the left doubly-bonded carbon clearly holds two different groups. The right doubly-bonded carbon is considered to hold two groups because in traversing the ring in opposite directions the ring-groups appear in different order. Consequently, this compound has a geometric isomer which is shown at the bottom of the page.

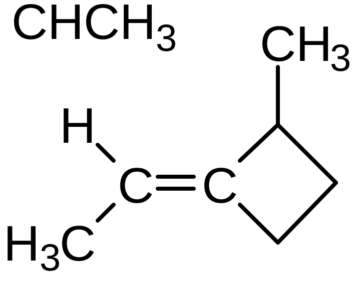


1 = CHCH$_3$,
2 = CH$_2$,
3 = CH$_2$

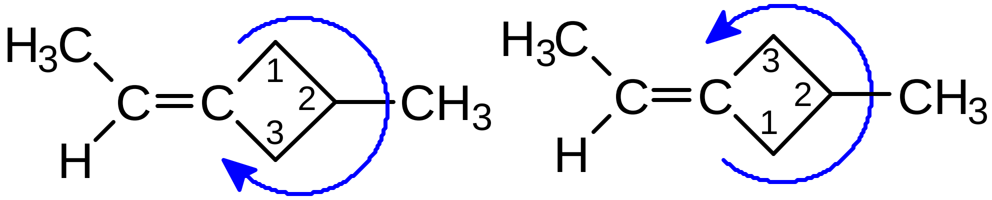


1 = CH$_2$,
2 = CH$_2$,
3 = CHCH$_3$

The geometric isomer is



On the other hand, the compound shown below does not have a geometric isomer because in traversing the ring on the right we find that the ring-groups are in the same order whether we go clockwise or counterclockwise.



1 = CH_2,
2 = $CHCH_3$,
3 = CH_2

1 = CH_2,
2 = $CHCH_3$,
3 = CH_2

There is no geometric isomerism here.

E, Z System for Naming Geometric Isomers —

Learn how to do this. It is covered on pgs. 83-86 in McMurry, “Fundamentals of Organic Chemistry,” 4th edition.

Classification of Reactions – by:

1) Functional group
2) Kind
    a) Addition: $A + B \longrightarrow C$
    b) Elimination: $A \longrightarrow B + C$
    c) Substitution: $A\text{-}B + C\text{-}D \longrightarrow A\text{-}C + B\text{-}D$
    d) Rearrangement: $A \longrightarrow B$,
    where B is a constitutional isomer of A
3) Mechanism
    a) General Type
    b) Specific Details

<u>General Mechanism Type</u>

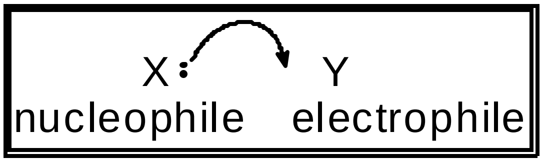
Two common reaction types –

± Polar

☯ Free Radical

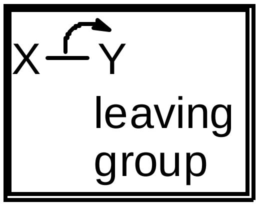
<u>Polar</u> – most important.

Bonds are formed *heterogenically*: an electron rich moiety (molecule or part of a molecule) called a *nucleophile* donates a pair of electrons to an electron poor moiety, an *electrophile*. Basically, a nucleophile is a Lewis base; an electrophile is a Lewis acid.

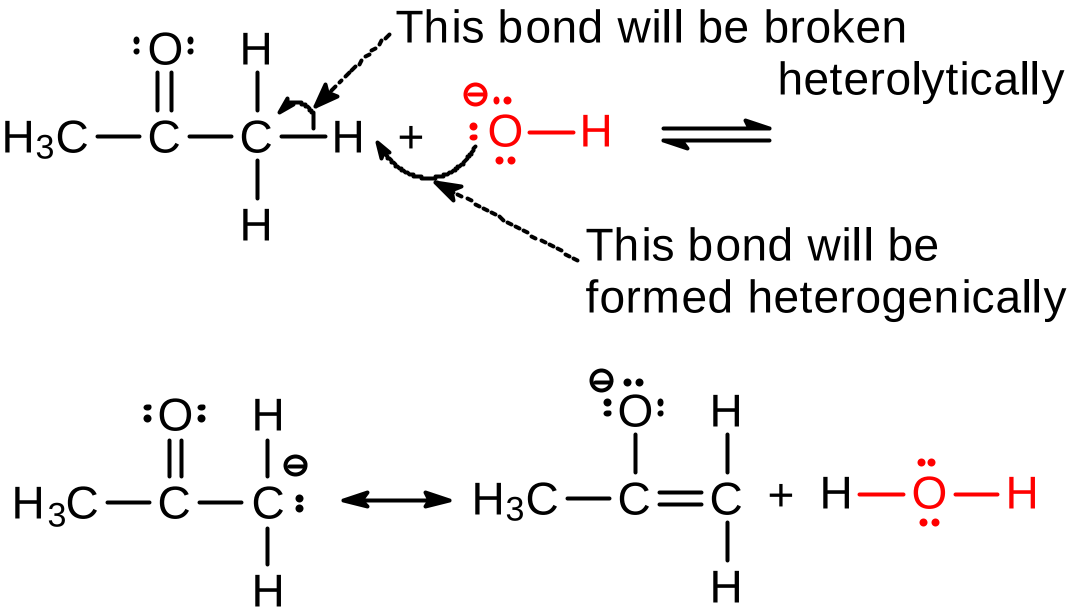


Bonds are broken *heterolytically*: one part of a molecule accepts both electrons in bond as it is broken.

When a single bond is broken the departing moiety is called the *leaving group*.



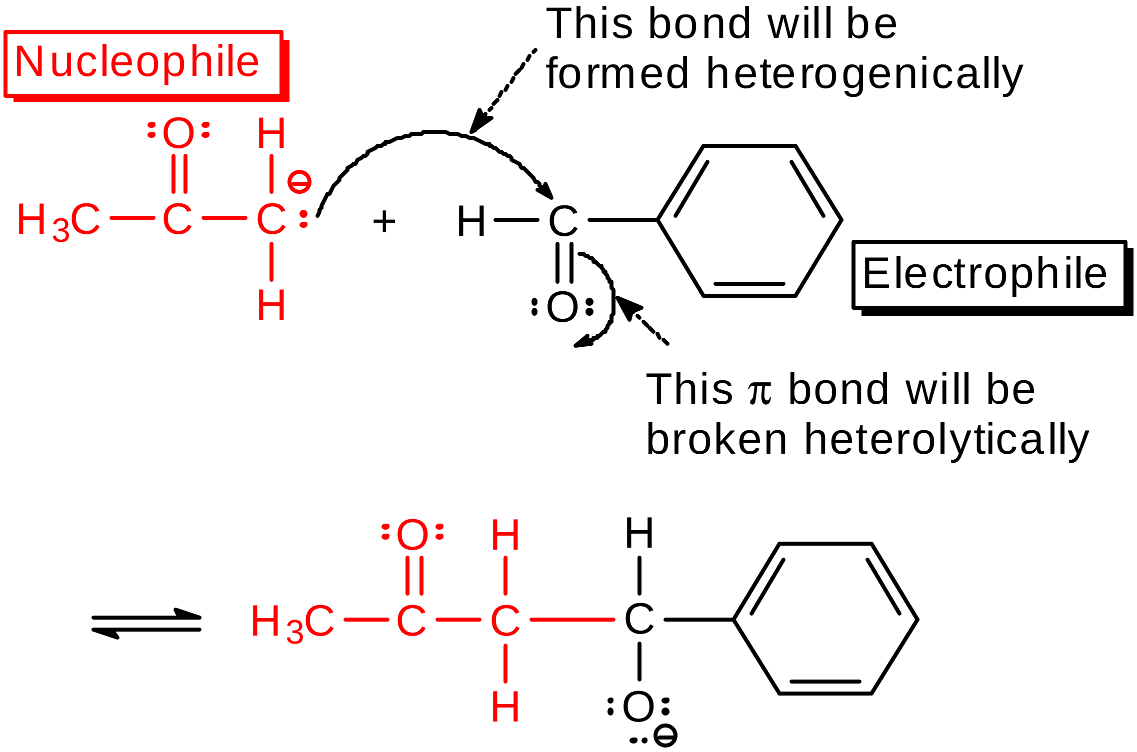
Examples of polar reactions:



This bond will be broken heterolytically

This bond will be formed heterogenically

When C is site of attack,
Lewis base = *nucleophile*
Lewis acid = *electrophile*



(Free) Radical –

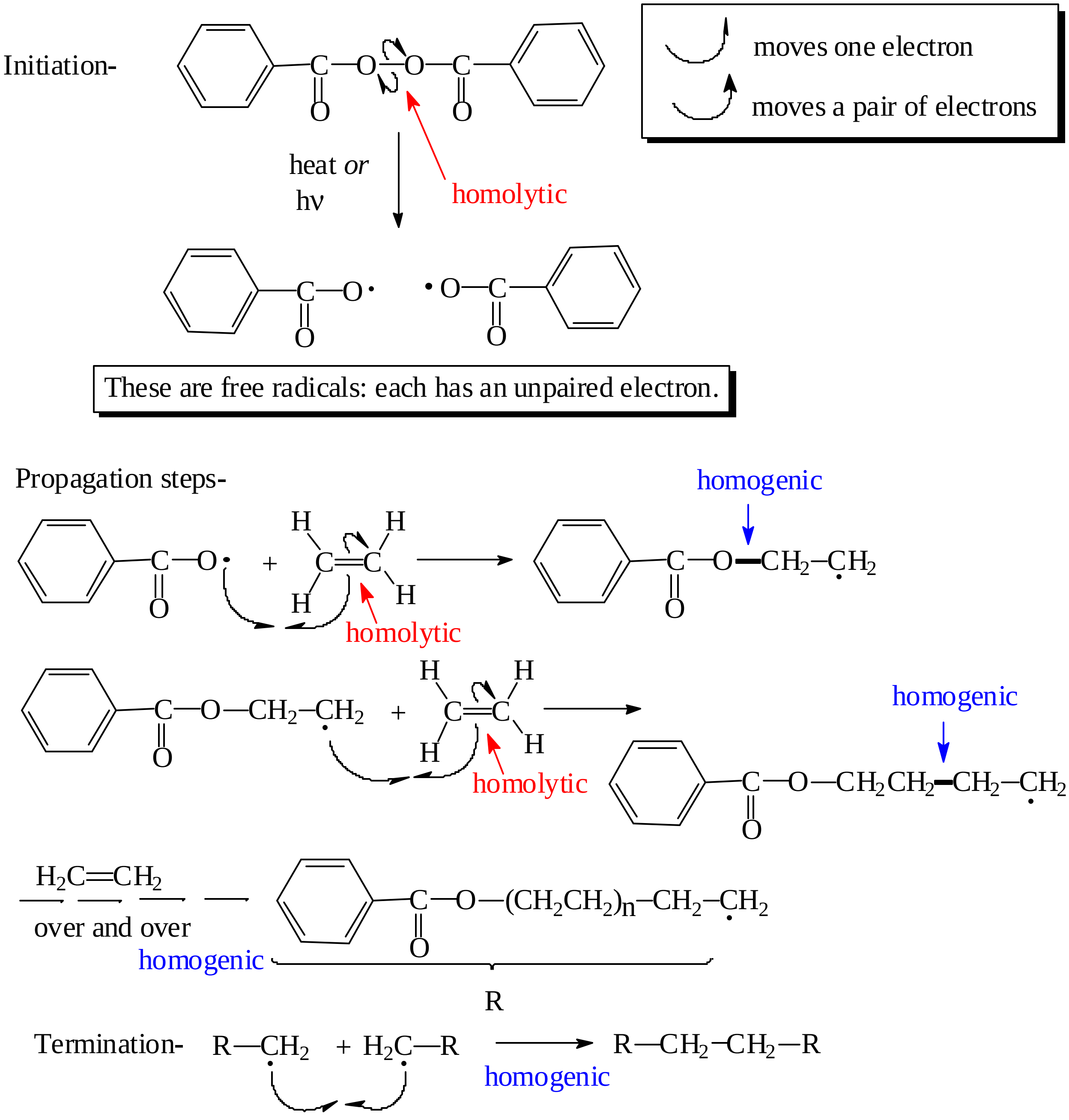
Reaction involves a *(free) radical* --- a chemical species with an unpaired electron.

Bonds form *homogenically*: radical and moiety with which it reacts each provide **one** electron.

Bonds break *homolytically*: atom on each side of bond takes **one** electron from bond.

Example: Polymerization of Ethylene to Form Polyethylene

This is a *chain reaction.* The product of each step, a free radical, is a reactant in a subsequent step.



Reaction Equilibrium

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

$$K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

$K_{eq} = e^{-\Delta G°/RT} = 1/e^{\Delta G°/RT}$,

where, R = 1.99 cal/degree-mole
T = temperature in ^{o}K

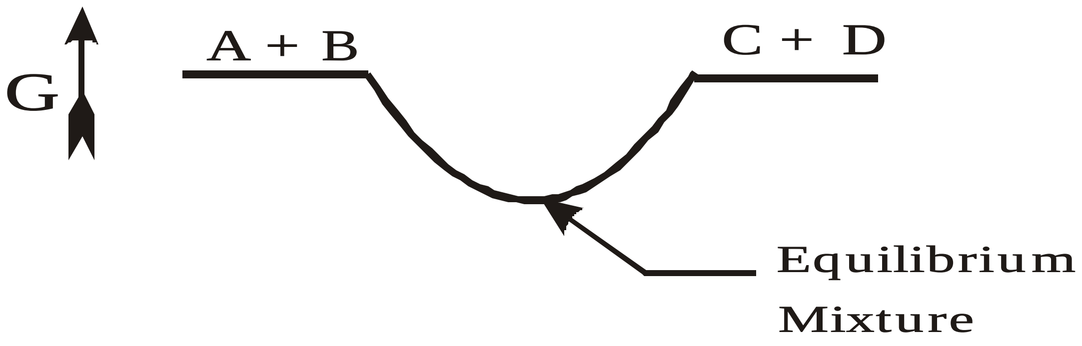
$\Delta G°$ = the standard Gibbs free energy change
= $G°_{products} - G°_{reactants}$

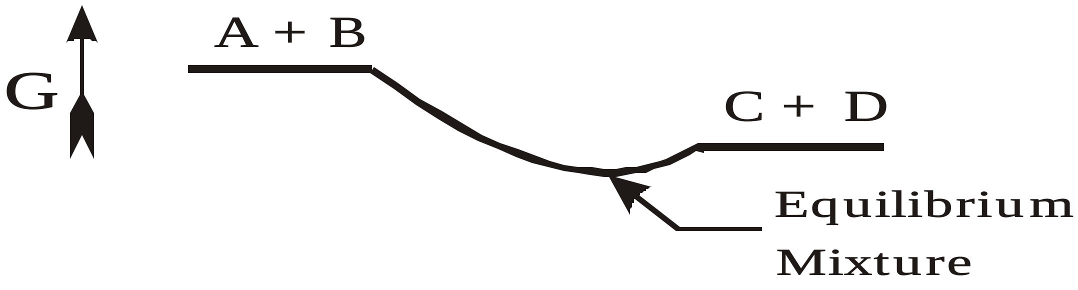
[For the moment let's not worry about exactly what "Gibbs free energy" is. We'll get back to this. For the moment let's just agree that both reactants and products contain some kind of energy that we call Gibbs free energy.]

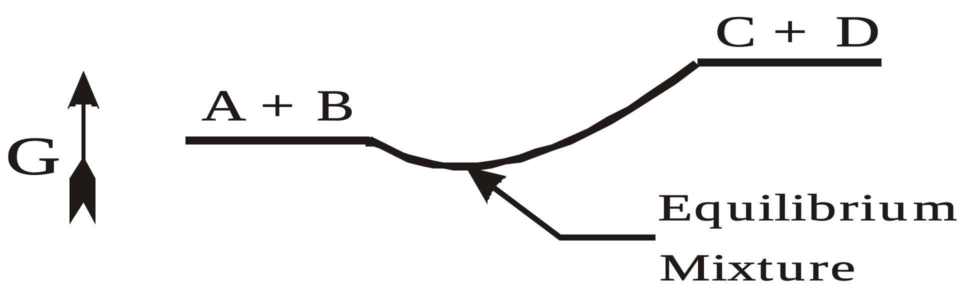
If $\Delta G^o = 0$, $K = 1$. The larger ΔG^o is, the smaller K is; the smaller or more negative ΔG^o is, the larger K is.

(If $G^o_{products} > G^o_{reactants}$, $K < 1$, reactants favored at equilibrium;

if $G^o_{products} < G^o_{reactants}$, $K > 1$, products favored at equilibrium.)







$\Delta G^o = \Delta H^o - T\Delta S^o$

ΔH^o = standard heat of reaction;

If negative the reaction is *exothermic*; heat is given off by the reaction and the products have less H^o (energy) than the reactants.

If positive the reaction is endothermic; heat is absorbed by the reaction and the products have more H^o (energy) than the reactants.

ΔS^o = standard change in entropy and is a measure of the amount of "disorder" or "randomness" caused by a reaction.

In many cases, especially at room temperature, $T\Delta S^o$ is small compared to ΔH^o. In these cases, ΔG^o **.** ΔH^o; we will ordinarily make this assumption. So, if a reaction is exothermic, $K_{eq} > 1$, and if it is endothermic, $K_{eq} < 1$.

Reaction Rate

Reaction rate refers to how fast or slow a reaction is: how fast a product forms or a reactant disappears. Mathematically the rate is: d[product]/dt or -d[reactant]/dt, where [ ] is concentration and t is time.

It is often the case that reactions with a favorable equilibrium constant are fast, but not always. It is almost always the case that reactions with unfavorable equilibrium constants are slow.

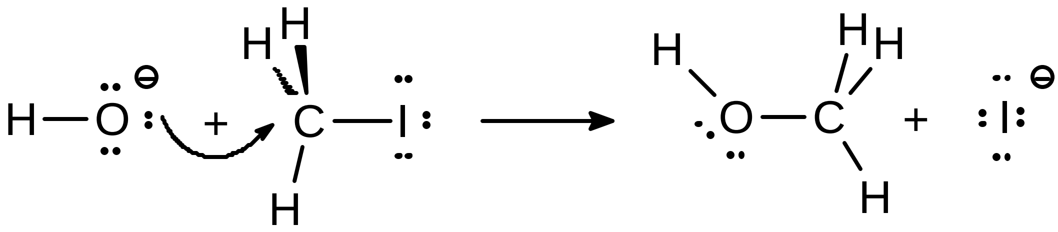
An overall reaction – reactants º products – may comprise several steps or only one. The rate of the overall reaction cannot be faster than the slowest step – the *rate limiting step*. The rate of any step, including the rate limiting step is the product of 3 factors: molecular collision frequency, energy exchange in collision, and a probability factor.

Molecular collision frequency – Molecules (or atoms or ions) have to collide in order to react with each other; the more collisions per unit time, other things being equal, the faster the reaction. In most cases not every collision will result in reaction; this is where the other two factors come into play.

Energy factor – To react, colliding molecules must usually exchange some energy, which means they must bang into each other with a certain amount of force. For example, if a reaction involves breaking one bond (#1) and forming another (#2), the energy required to break #1 will come partly from the energy released by formation of #2. However, kinetic energy is needed from the collision because bond breaking (#1) and bond formation (#2) are not perfectly synchronized or because bond #2 is weaker than #1.

The minimum energy required from the collision for reaction to occur is called e_{act} or $\Delta H^{\ddagger}$.

Probability factor – This depends on the orientation of the molecules when they collide and on the change in "randomness" at collision. The orientation part is pretty straightforward. Consider the following reaction:



The fact is, for this reaction to occur, the oxygen of the OH group must hit the carbon of the iodomethane on the side away from the iodine. If the collision occurs in any other orientation – the oxygen of the OH hits a hydrogen or the iodine, or the H of the OH hits any of the atoms in the iodomethane – the reaction will not take place.

The "randomness" part of this factor is a little esoteric and we will not consider it further.

$$\text{Rate} = \underbrace{\text{Collision Frequency}} \times \underbrace{\text{Energy Factor}} \times \underbrace{\text{Probablility Factor}}$$

Depends on concentration and temp.

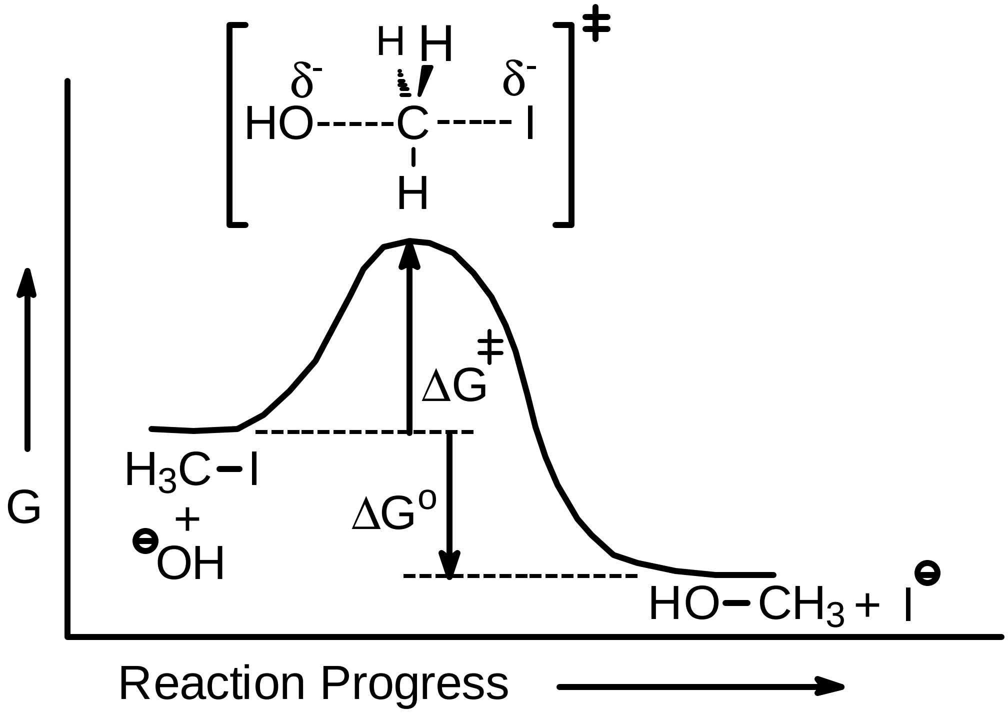
Most important; depends on $\Delta H^{\ddagger}$ (~ e_{act}) and T; fraction of collisions with
$e \geq e_{act} = \exp -e_{act}/RT$.

Depends on orientation and "randomness": $\Delta S^{\ddagger}$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

Consider –

$$CH_3I + {}^{\ominus}OH \longrightarrow CH_3OH + I^{\ominus}$$



This is a fairly simple reaction. The reactants, iodomethane and hydroxide ion, form the products, methanol and iodide ion, in one step. Since the C-O bond is stronger than the C-I bond more energy is released than consumed, so ΔH^o is negative – the reaction is exothermic. Since $\Delta G^o \approx \Delta H^o$, it, too, is negative. Note, in the reaction energy diagram, that the products are below the reactants in terms of G, the free energy.

Note, also, in the reaction energy diagram that the colliding molecules must change enough kinetic energy from the collision into potential energy to “get over” the $\Delta G^{\ddagger}$ barrier. The molecular structure at the highest point in the energy curve, shown in brackets with a double dagger (‡), is called the *transition state.* This is not a stable (or even an unstable) molecule. It is the highest energy arrangement of atoms through with the reactants pass on their way to forming products. At this point in the reaction the C-I bond is partially broken and the C-O bond is partially formed. As the reaction continues, the C-I bond is broken and the C-O bond is formed, giving the products.

Some reactions are more complicated than this one. As an (important) example, some reactions follow the path: reactants $\rightarrow$ [transition state 1]‡ $\rightarrow$ intermediate $\rightarrow$ [transition state 2]‡ $\rightarrow$ products. An instance of this would be the reaction between an alkene and HBr to give an alkyl bromide. The reaction energy diagram in this case will exhibit two “humps” – the two transition states – and a high-energy valley between them – the *carbocation* intermediate. This case is discussed at length in McMurry.