# Fundamentals of Theoretical Organic Chemistry

Lecture 6

2.1.2 Electrophilic addition

The electophilic addititon is one of the most important basic reactions in chemistry. In general, addition falls into two main subreactions such as electrophilic and nucleophilic addition. The name is given since two reactants join forming a single product, in other words they are added together without having "vice-products". The two subgroups are separated on the observation in that of one of the reactants attacks on the other, bulkier molecule whether the "attacker" molecule has a behaviour of an electrophilic or nucleophilic. Thus, if it is a positively charged (fully or partially) molecule, we term it electrophilic (electron and philos), while if it is a negatively charged (fully or partially) molecule, we call it nucleophilic (nucleus and philos) addition. The most important reactions of electrophilic additions are described throughout the following chapters.
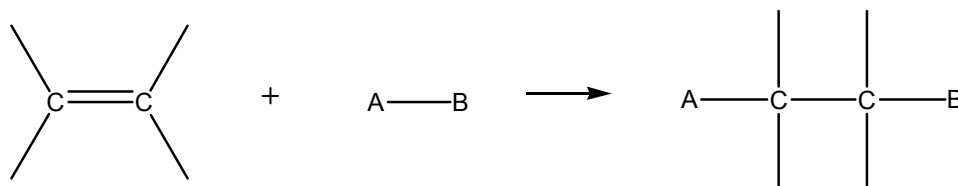

Figure 2.1.2-1. An electrophilic addition is between two reactants

One of them contains an unsaturated, double bond(C=C), while the other one (A–B) has a partially or entirely positively charged group, A in the example given above (electrophilic). A can be H^+, Lewis acid, metal ions (Ag^+), or a partially positive Br. B can be a Lewis base or a halogenid. If A–B is not a polar molecule, then the single bond between them (σ) should be polarizable (this will ease the reaction). This is well known that electrons of the σ-bond are under larger nuclear attraction than electrons on π-orbitals. Therefore, π-electrons are observable at a larger distance from the two carbon atoms in sp^2 hibridization state. This results in a larger chemical reactivity than the electrons of σ-bond. The prelude of the electrophilic addition is an interaction between this electron-rich bond with an electrophilic atom. The reaction can easily be represented by cancellation of a π– and a σ-bond and a production of two σ-bonds. According to this, energetically an electrophilic addititon is an exotermic mechanism that is due to the energy difference of the σ- and π-bonds.

Composition of the other reactant (A–B) also determines two main subreactions. These may be symbolized as H–Z (such as H–Br) and the other as Z (such as Br_2).

Addition of H - Z to >C = C<

The mechanism is the same for this addition reaction no matter what the structure of Z may be.
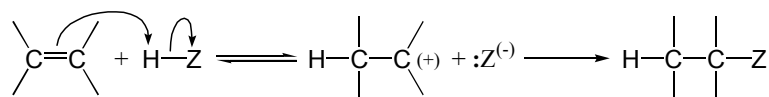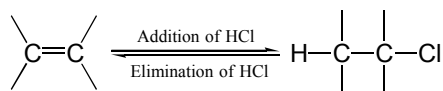

2.1.2-1.

The following H - Z structures may be considered:

H-Cl, H-Br, H-I, H-OH$_2^{(+)}$, H-OSO$_3$H, etc

2.1.2-2.

Note that the addition of these reagents to the carbon-carbon double bond is the reverse of the elimination reactions.

2.1.2-3

It should be emphasized that there is a carbocationic intermediate in reaction in 2.1.2-1. and this species may undergo skeletal rearrangement during the reaction, leading to an isomeric olefin product.

Markovnikov's rule applies when H - Z is added to a substituted carbon-carbon double bond
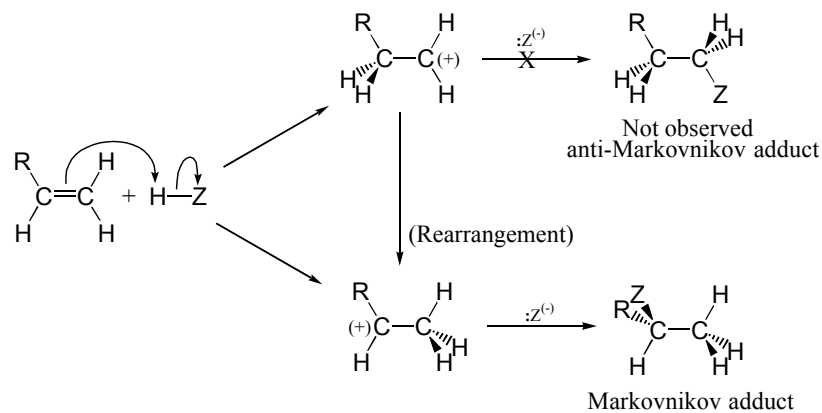
2.1.2-4.

Traditionally, the rule is formulated in terms of preference of attachment i.e., the H is attached to the least substituted carbon (or equivalently, the Z is attached to the most
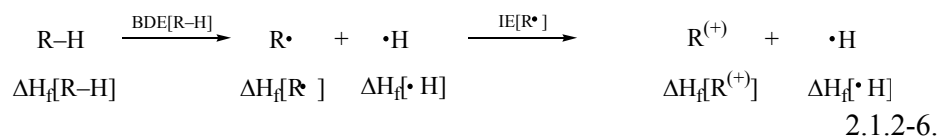
substituted carbon). We know, today, that the stability of the intermediate carbocation is the underlying cause of Markovnikov's rule. Of course Markovnikov could not formulate his rule by saying that if there are two alternatives the most stable carbocation is formed since in 1870, carbocations were not known to exist, in fact even the electron was not discovered by J. J. Thomson until 1897.

Previously we showed the following order of carbocation stability:

$$3° > 2° > 1° > Me^{(+)}$$

2.1.2-5.

which was rationalized in terms of hyperconjugation. Some quantitative information is presented below to underline the above principle.

We may look at thermochemical data such as bond dissociation energy (BDE) and ionization energy (IE) as arithmetical differences between enthalpies of formation.

$$R–H \xrightarrow{BDE[R–H]} R\bullet + \bullet H \xrightarrow{IE[R\bullet]} R^{(+)} + \bullet H$$

$$\Delta H_f[R–H] \qquad \Delta H_f[R\bullet] \quad \Delta H_f[\bullet H] \qquad \Delta H_f[R^{(+)}] \quad \Delta H_f[\bullet H]$$

2.1.2-6.

$$BDE[R–H] = \Delta H_f[R\bullet] + \Delta H_f[\bullet H] - \Delta H_f[R–H]$$

2.1.2-7.

$$IE[R\bullet] = \Delta H_f[R^{(+)}] - \Delta H_f[R\bullet]$$

2.1.2-8.

The various enthalpies of formation for selected species are summarized in Table2.2.1.-1**Hiba! A hivatkozási forrás nem található.**. It is clear from this table that alkyl substitution stabilizes all three types of species R - H, R• and R (+). However, the extent of stabilization is the greatest in the case of the cations. From the last line of Table 2.2.1.-1.we can see the average of one methyl stabilization as one goes from Me to ^{t}Bu. Using round figures, the average one Me substitution shows the following progression of stabilization in units of Kcal/mol.

Species	R-H	R·	$R^{(+)}$
Enthalpy(Kcal/mol)	4	8	32

Table 2.1.2-1. Approximate enthalpies of formation of selected saturated hydrocarbons, free radicals and carbocations.

Molecule	ΔH_f(kcal/mol)		
	R - H	R●	R(+)
$CH_3–H$	-18	+35	+261
$CH_3–CH_2–H$	-20	+28	+216
$CH_3–CH_2–CH_2–H$	-25	+23	+211
CH₃ H—C—H CH₃	-25	+21	+191
CH₃ H₃C—C—H CH₃	-32	+12	+166
$\Delta\Delta H_f=\Delta H_f^{(t-Bu)} - \Delta H_f(Me)$	-14	-23	-95
$(\Delta\Delta H_f)/3$	-4.67	-7.67	-31.67

Note: ΔH_f (H●) = +52 Kcal/mol

The three combined enthalpy levels presented in [8.8] i.e. ($\Delta H_f[R(+)] + \Delta H_f[●H]$), ($\Delta H_f[R ●] + \Delta H_f[●H]$) and $\Delta H_f[R - H]$, are shown for several species in next figure.
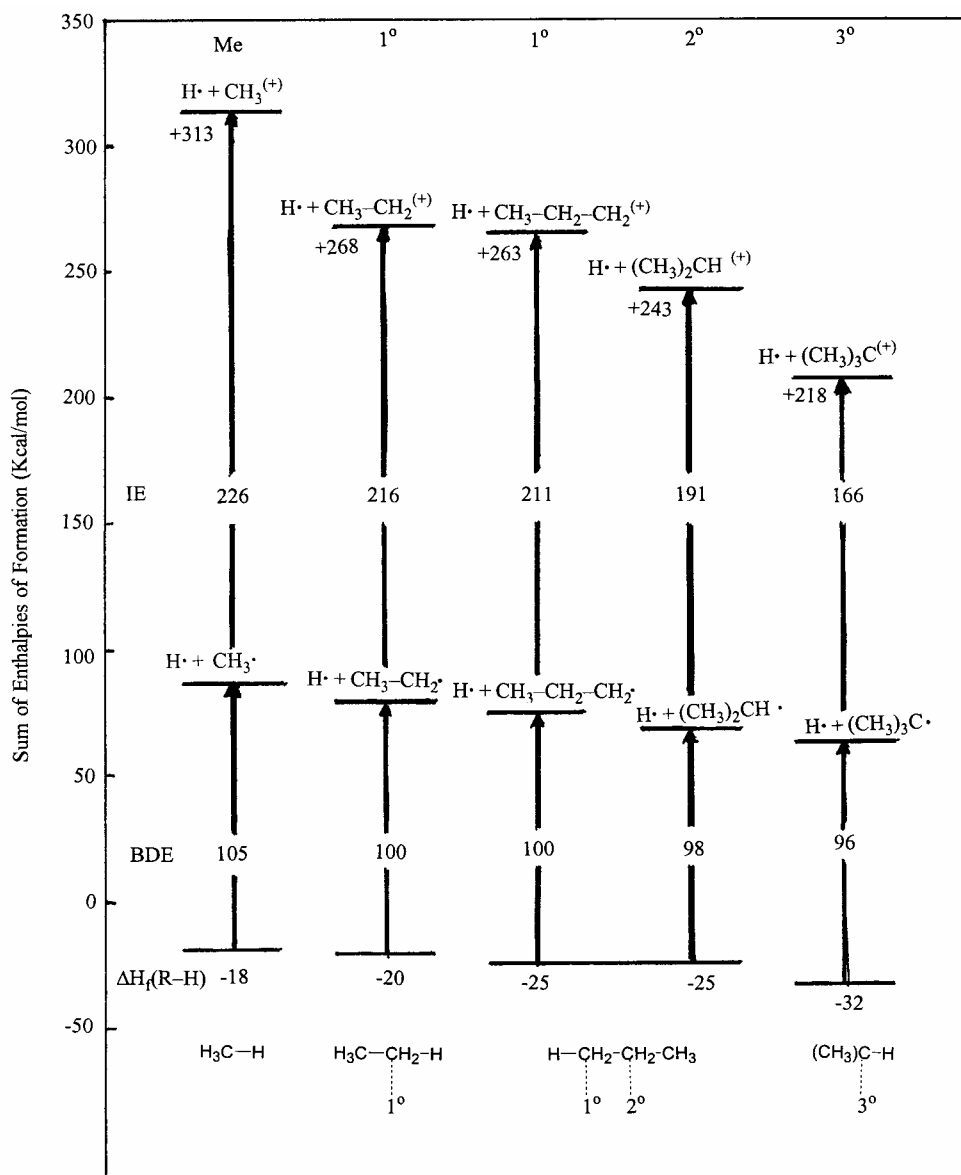
Figure 2.1.2-2. Enthalpy levels of the following process: R - H → R• + •H →R(+) + •H for various alkyl groups (R).

The relative stability of 3°, 2°, 1° and CH_3^+ carbocations may be calculated relative to R•, according to equation 2.2.1.-7, in terms of the radical ionization energy.

Nowadays, slightly more accurate data are available from the work of Houle and Beauchamp [J.A.C.S. 101 (1979) 4071.].

**Table 2.1.2-2. Recommended thermochemical data [kcal.mol⁻¹] for R• and R⁺.**

R	ΔH_f (R•)	ΔH_f (R⁺)	PA (olefin)
Me•	34.9	261.8	—
MeCH₂•	25.7	219.2	159.0
Me₂CH•	17.6	187.3	183.3
Me₃C•	8.4	162.9	198.5

On the basis of the above, it is not difficult to predict where $H^{(+)}$ attack is most likely when the following diene is subjected to, let's say, H - Br addition.
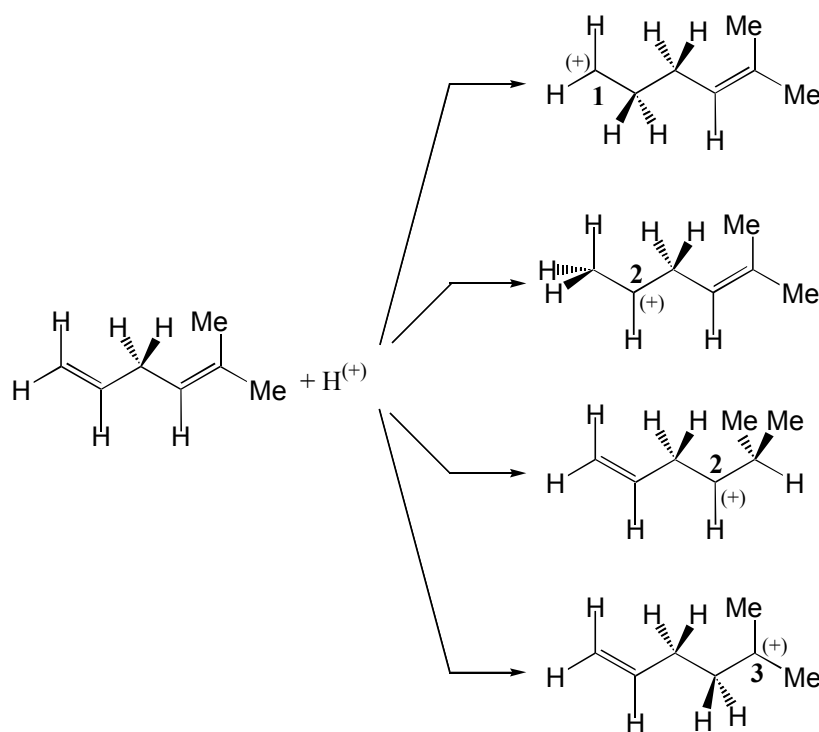

2.1.2-9.

Clearly, the 3° carbocation 2.2.1.-10 is the most stable, the 1° carbocation is the least stable and the two 2° carbocations, and are nearly equivalent and in between the two extremes. This implies three types of reaction energy profiles: the lowest one will be for the 3°, the next higher for two 2°, and finally the highest for the 1° carbocation, as illustrated in next figure
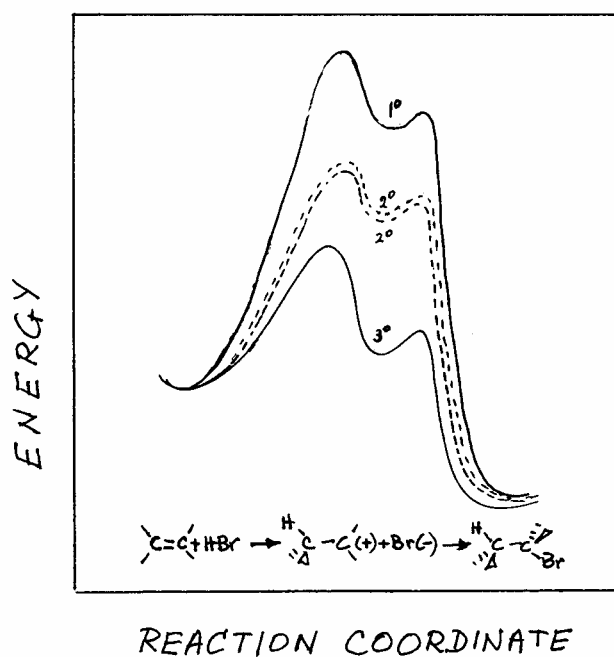
Figure 2.1.2-3. A schematic illustration of the energetic basis of Markovnikov's rule for 1°, 2° and 3° carbocations.

Markovnikov's rule is therefore, a consequence of kinetic preference, which in turn is a consequence of the thermodynamic stability of the intermediate carbocations.

In general, Markovnikov's rule is always obeyed. In the presence of some peroxides (e.g. HO-OH), however, H-Br adds across the double bond in an anti-Markovnikov fashion.
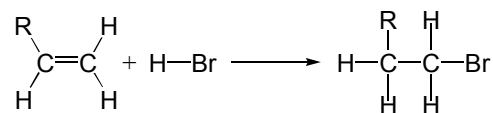
2.1.2-10.

Finally, it should be mentioned that the planar carbocationic intermediate may be attacked by the nucleophile $:Z^{(-)}$ from the two sides [2.2.1.-12]. Thus, even if a stereocentre is created by an addition, a racemic product mixture is obtained.
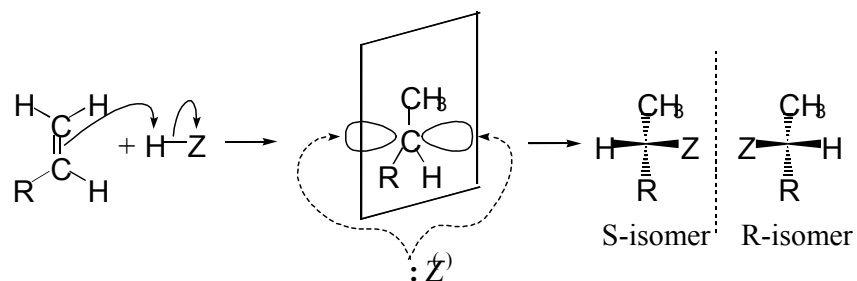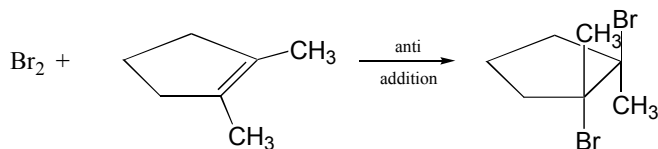

2.1.2-11.

Addition of Z2 and YZ to >C=C<

The addition of H_2 to a carbon-carbon multiple bond on the surface of a catalyst (Pt or Pd) leads to syn addition . In the case of a ring structure, the syn addition of $Z_2 = H_2$ gives a cis-product [2.2.1-13].
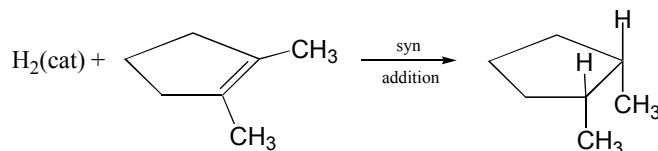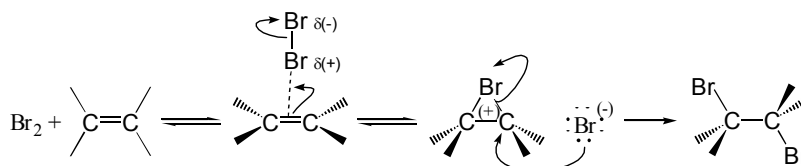

2.1.2-12.

In contrast to the above, halogen addition ($Z_2 = Cl_2$ or Br_2) must proceed by anti addition because the adduct is trans.
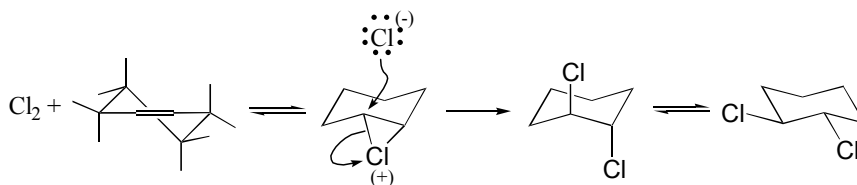

2.1.2-13.

The mechanism of the dihalogen addition reveals that the two halogen atoms do not add at the same time. In fact, they do not add as atoms but as ions in an anti fashion as shown below.
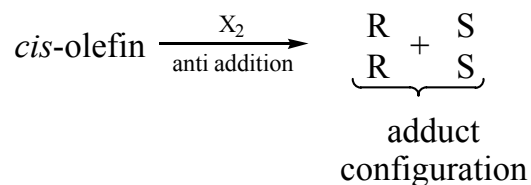

2.1.2-14.

Of course the mechanism is the same for the addition of Cl_2.
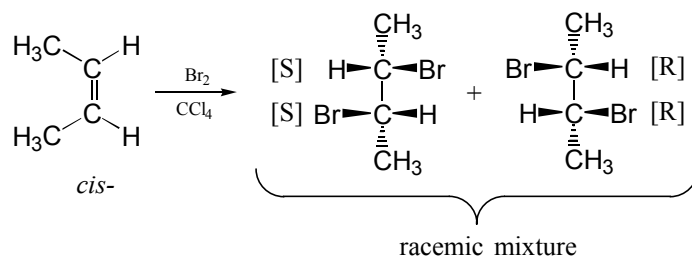

2.1.2-15.

Through these addition reactions (c.f. 2.2.1-14 - 2.2.1-16]) we have created two chiral centers. Knowing that the trans–1,2–disubstituted ring structures can be (R,R) and (S,S) and

knowing that cyclic olefins are cis-geometrical isomers, we can conclude that the following stereochemical relationship applies:
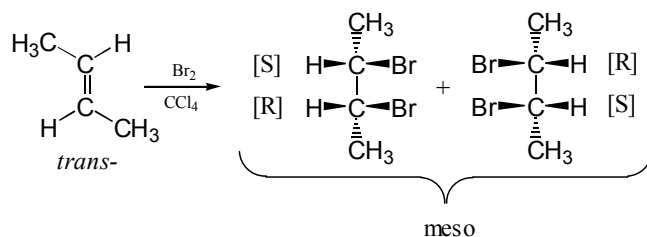
$$cis\text{-olefin} \xrightarrow[\text{anti addition}]{X_2} \underbrace{\begin{array}{ccc} R & & S \\ & + & \\ R & & S \end{array}}$$

adduct
configuration

2.1.2-16.

Applying this principle to open chain alkenes we find the following:
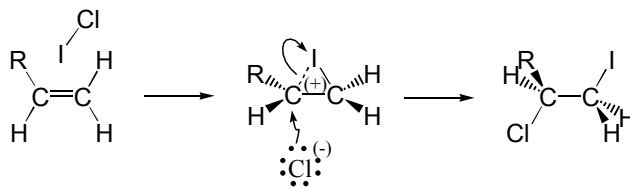

racemic mixture

2.1.2-17.

meso

2.1.2-18.

In the case of Cl$_2$ and Br$_2$ addition, Markovnikov's rule makes no sense since both fragments are the same. However, in the case of interhalogen compounds, such as $^{\delta(+)}$I–Cl$^{\delta(-)}$, Markovnikov's rule does apply.
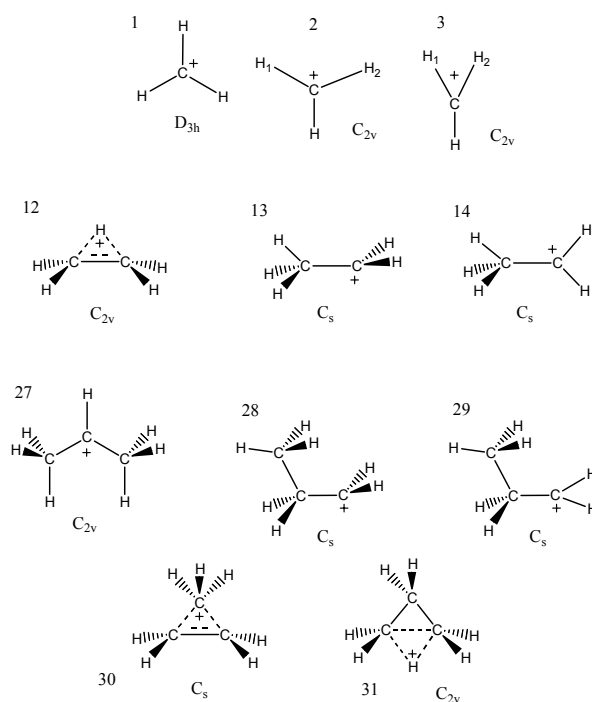

2.1.2-19.

The epibromoniom ion [2.2.1-18] or epichloronium ion [2.2.1.-19] may react with any other nucleophiles present. These nucleophiles may be added to the reactant, e.g., N$_3^{(-)}$, or they could be nucleophilic solvents e.g., H$_2$O or CH$_3$OH.
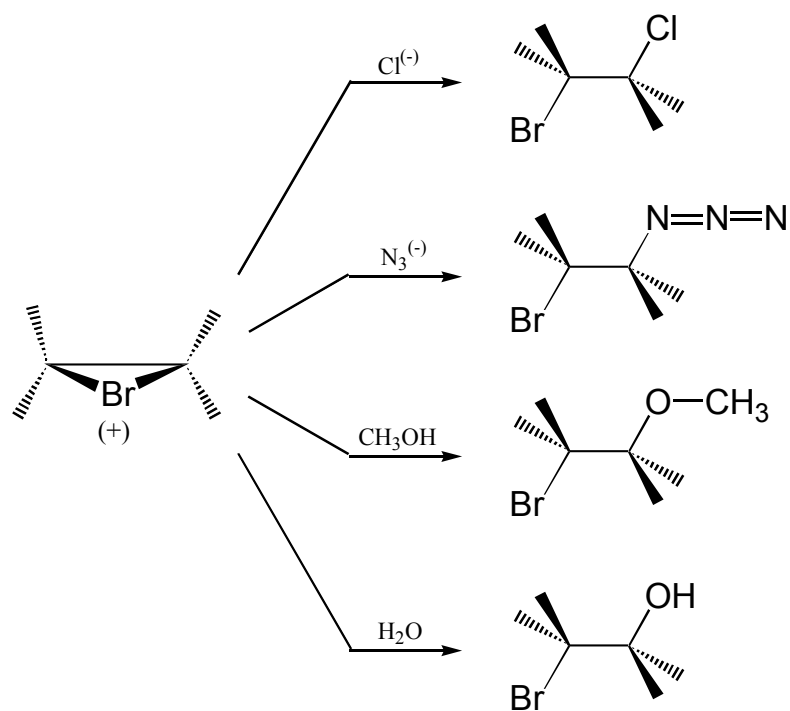
2.1.2-20.

In one of the earliest studies on the stability of carbocations was published in 1981 and achieved by computational approach. This is crucial in studying reactions (and products) that possess carbocation intermediates. Stability of different carbocations is related to the order of the carbon atom that carries the positive charge (see figures).
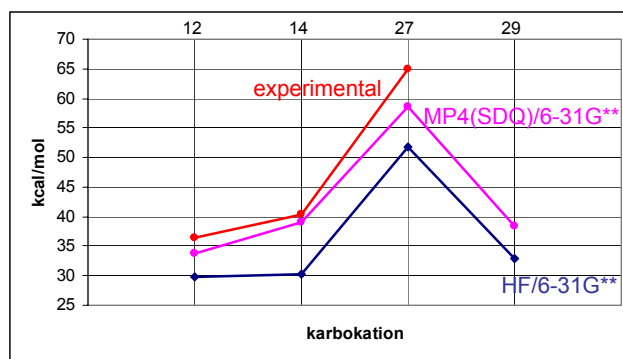
Figure 2.1.2-4. Stabilizációs energia (CH3+)

A somewhat stable carbocation intermediate during an electrophilic addition is not a question any more however the behaviour of the transition state that is formed before the intermediate is still highly enigmatic. For example, to date there are three supposed paths for bromination of an alkene. These are different in the way how the halogen (brome) is polarized.
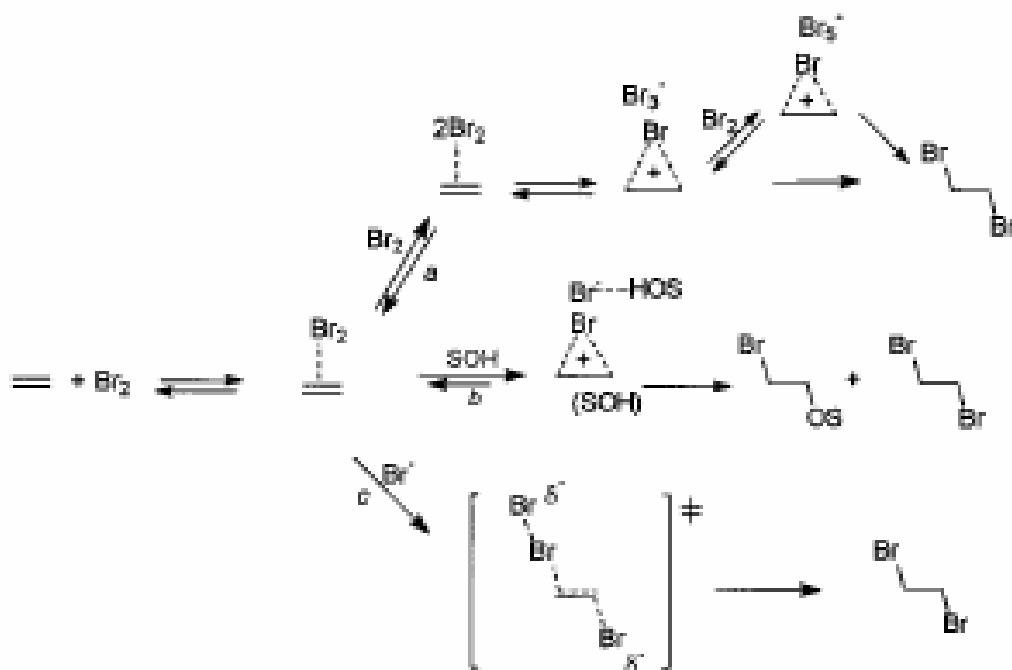
It is important to mention that fluorination follows an alternative way toward the addition of halogens to an alkene. This strongly supports the observed syn-addition of Fl_2 to alkenes (similar to H_2 addition) and not anti-addition as it is seen in case of other halogens (see figure for the supposed geometries).
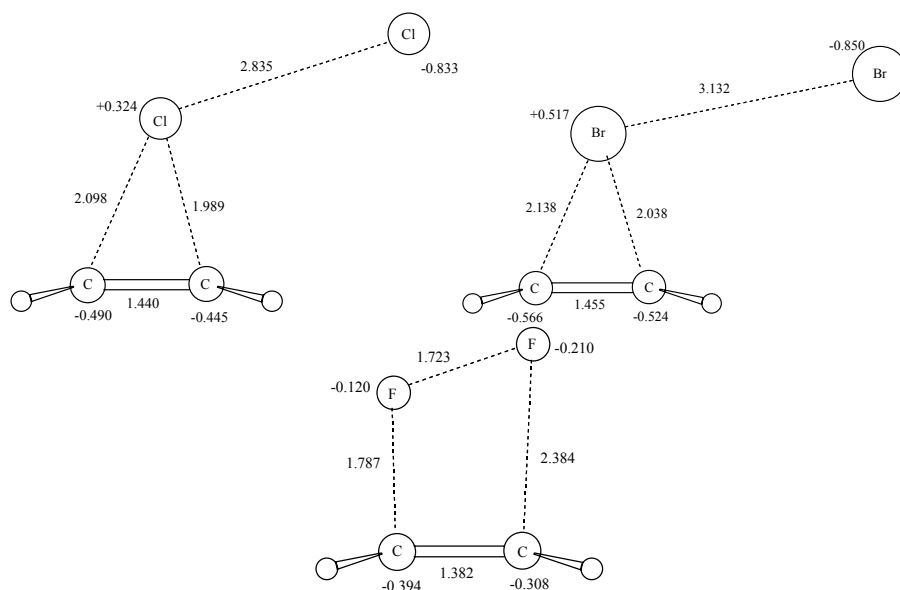
Figure 2.1.2-5. The energetic profile of such paths was already calculated on the similar reaction such as ethylene chlorination and can be drawn as Potential Energy Curves or Potential Energy Surface.
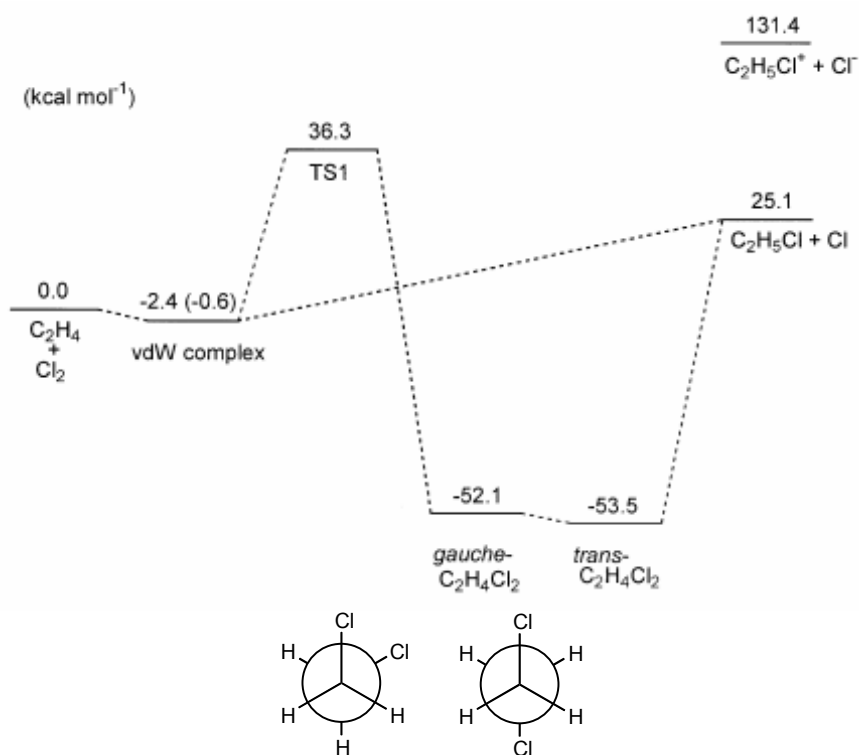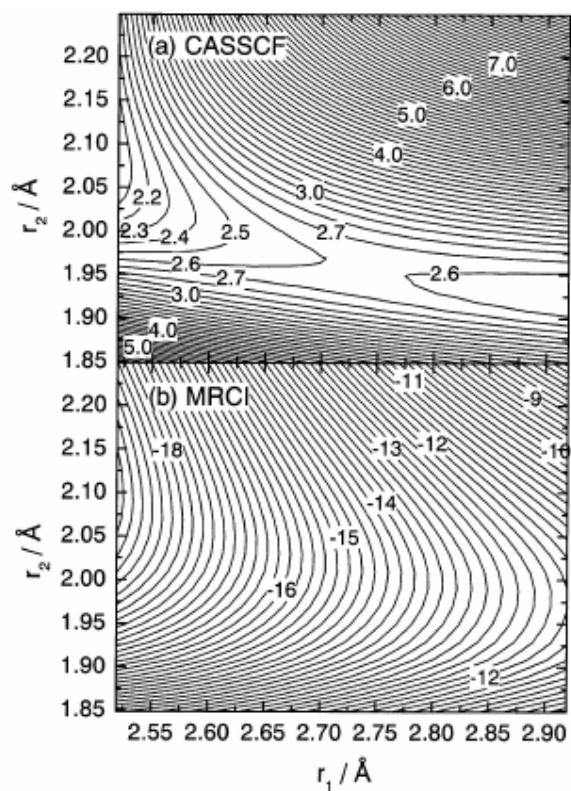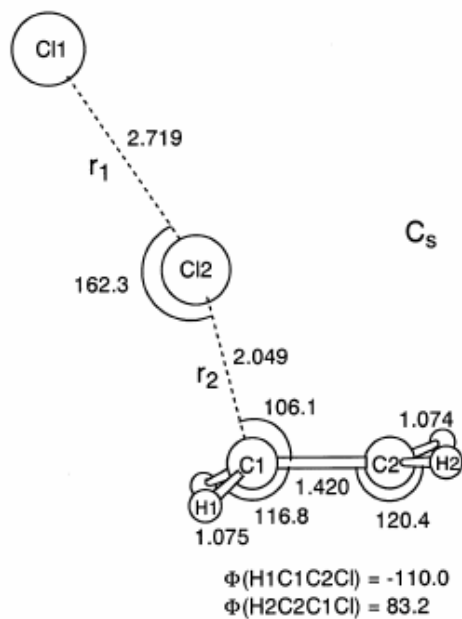

Figure 2.1.2-6. The values in brackets are BSSE corrected energies at PMP4(SDTQ,full)/6-311++G(d,p)//MP2(fc)/6-31+G(d) + ZPE level of theory.

Except the pathway involves radicals, there might be a transition state during halogenations.The transition state and the most relevant geometrical parameters that describe

the energetic profile of the chlorination of an ethylene can be summarized on a Potential Energy Surface.

Cl1

2.719
r_1

C_s

162.3 Cl2

2.049
r_2

106.1   1.074

C1   C2 H2
1.420

H1 116.8   120.4
1.075

Φ(H1C1C2Cl) = -110.0
Φ(H2C2C1Cl) = 83.2

Although, no simple calculation in vacuum will represent the mechanism experienced in laboratory environment, these structures seem to be the only models for examining this process. This is thought of the effect of the highly important solvent or/and another halogen

molecule in polarizing halogens. Charge Transfer Complexes are important structures during these processes. The production of CTCs is via solvent or a trimolecular complex.
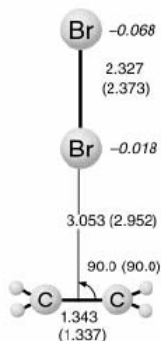
Computed energy for the complex in vacuum is about 145 kcal.mol^{-1} and seems to be too high for such a fast reaction. Due to solvent effect (dielectric constant) the predicted decrease is about 90 kcal.mol^{-1}. To this, hydrogen bonds decrease this value with additional 55 kcal.mol^{-1}. An alternative method for polarizing the halogen is via other halogen molecules. Thus, the trimolecular complex ($Cl_3{}^{-}$) eases the reaction by lowering the activation barrier by 30 kcal.mol^{-1}. In case of alkene halogenation, these predictions would justify an electrophilic addition via a TS.

However, this at least two-step-process can be drawn from a kinetic point of view. A k constant can be defined for the second step of the reaction: