Thermochemistry of reactive intermediates

Types of energy:

Internal energy, E, - sum of energies of all elementary particles of the system. Absolute internal energy- impossible to measure but possible to calculate quantum-mechanically.

Change in E at constant pressure and no work done- enthalpy, H. Experimentally- change in heat, ΔH

QM gives absolute H. H_0 =E + ZPVE; H_o= Enthalpy at zero Kelvin. Temperature correction, say to 298 K, will give H_{298} .

Gibbs energy, G=H-TS. Experimentally, ΔG could be measured. ΔG determines the position of equilibrium between the two states of the system

$$lnK_{eq} = - ΔG^0/RT$$

(The ^{0} symbolizes the standard states)

T=298K, P=1 Pa ≈ atm; 1 mol

ΔH <0 –exothermic, >0- endothermic

ΔG <0 –exergonic, sponataneous >0- endergonic, non-spontaneous

Stability- thermodynamic stability. Thermodynamically stable system corresponds to a minimum on the Potential Energy Surface (Profile)
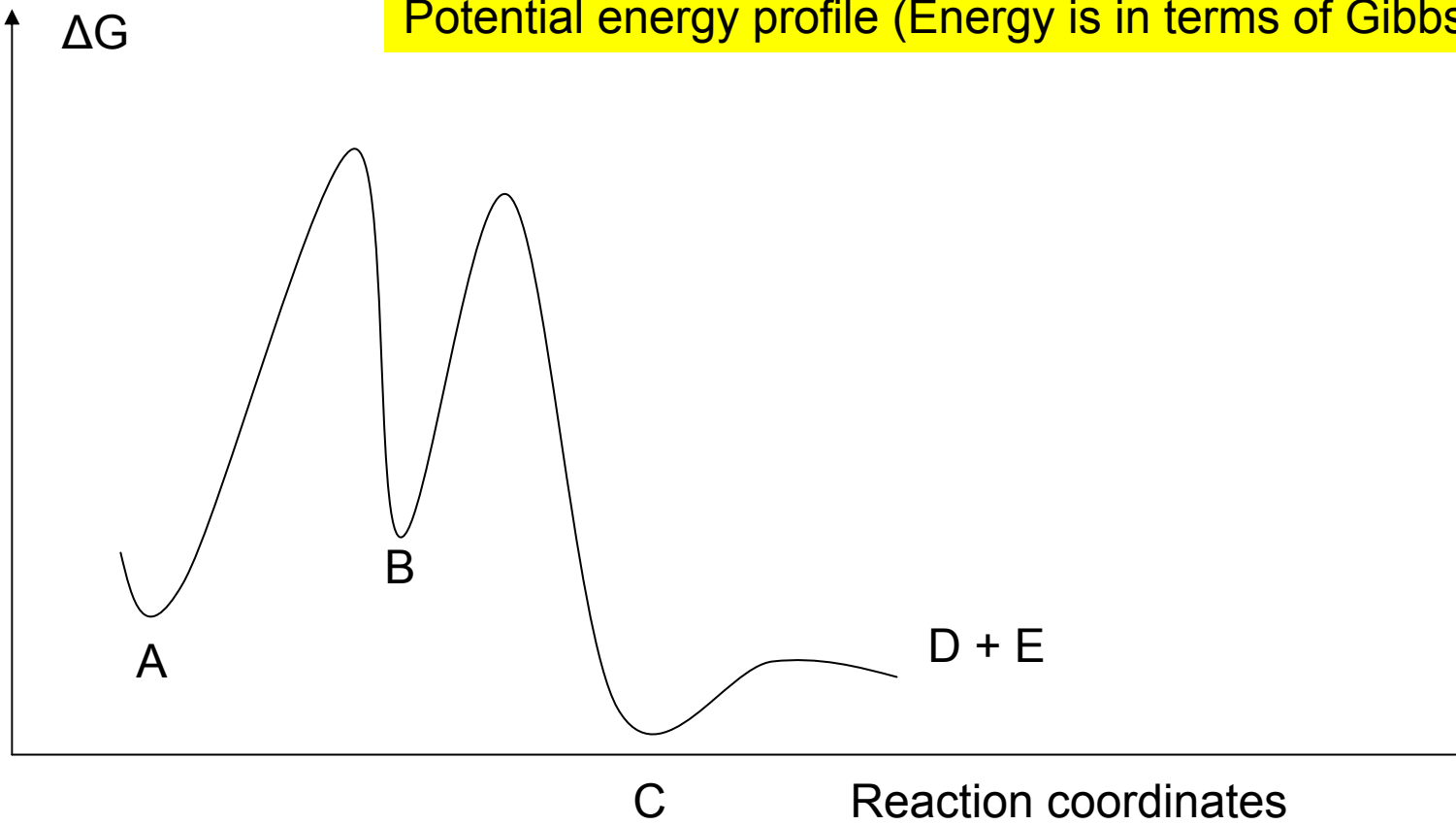
Stabilized- thermodynamically (ΔG) more stable than the reference system
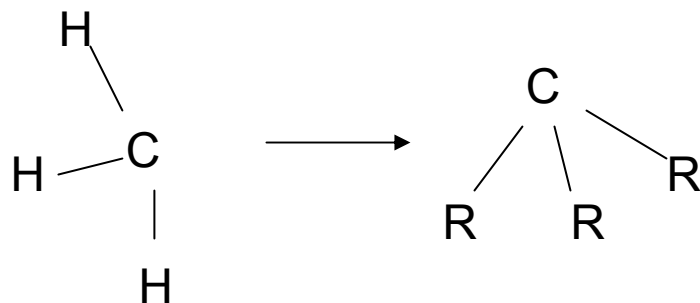
RADICAL IS STABILIZED BY R

Persistence- kinetics (barrier heights). Persistent- long lived

R-H → R• + H•   ΔH=BDE >0 ; the greater BDE, the less stable the radical

BDE, kcal/mol

	BDE, kcal/mol
H-CH_3	105.1
H-CH_2CH_3	98.2
H-$CH(CH_3)$	95.1
H-$C(CH_3)_3$	93.2
Ph-Ph	118

$3^0 > 2^0 > 1^0 >$ methyl

Vinyl and phenyl radicals are less stable than alkyl radicals, allyl and benzyl radicals- more stable due to hyperconjugation (resonance)
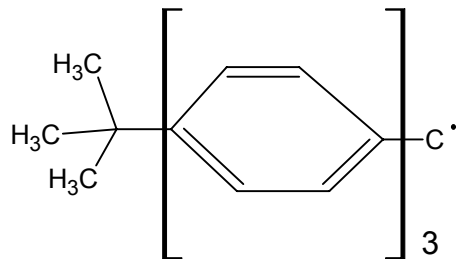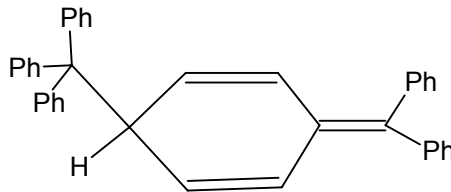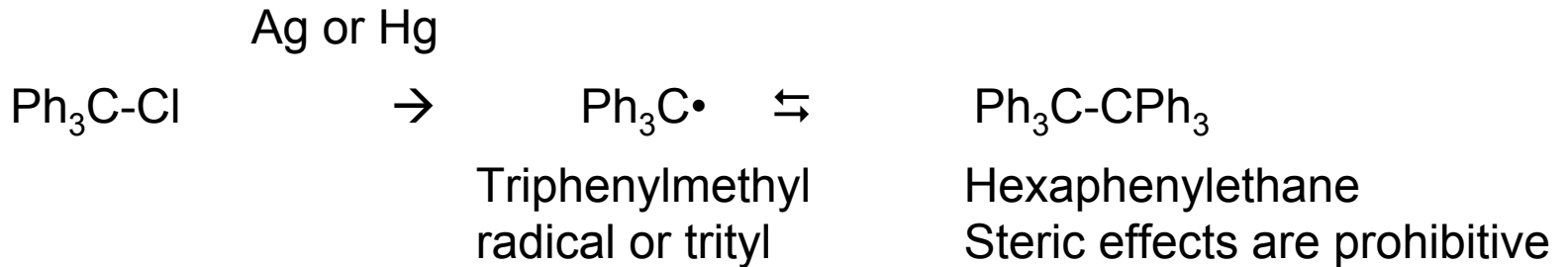
BDE are not really good measure for radical stability as it is also depends on stability of RH

BDE measure relative stabilities of radical with respect to the parent compound

For many series, there is no trends in BDE

1900, Gomberg

Ag or Hg

Ph$_3$C-Cl $\rightarrow$ Ph$_3$C• $\leftrightarrows$ Ph$_3$C-CPh$_3$

Triphenylmethyl
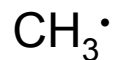radical or trityl

Hexaphenylethane
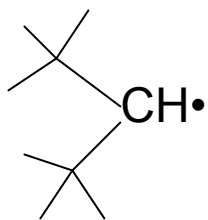Steric effects are prohibitive

No dimers- steric effect

For radicals, steric protection is more important for persistence than electronic effects

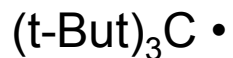Persistence in fluid solution, 10^{-5} M, 25 C^0, $t_{1/2}$

CH$_3\cdot$ 20 µs (longer in the gas phase!)

CH•   1 min

(t-But)$_3$C •   8.4 min

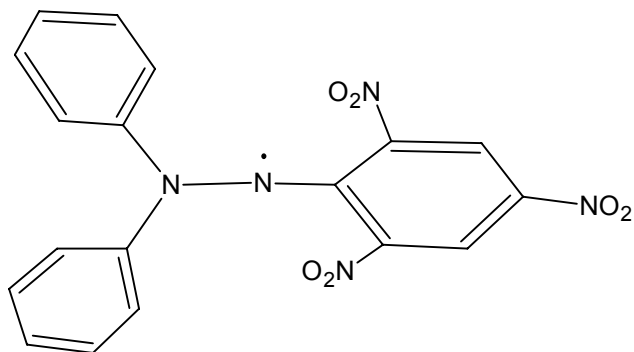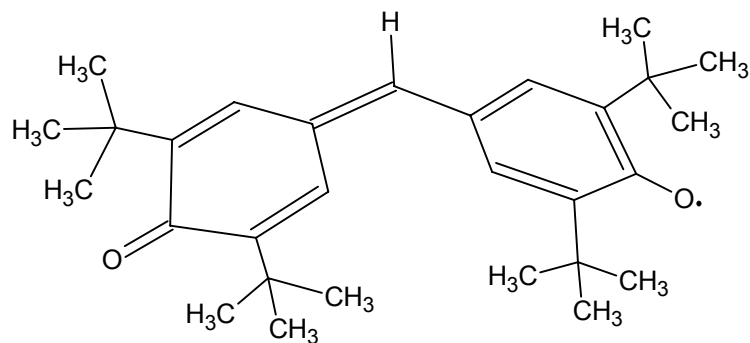(Me$_3$Si)$_3$C •   2.3 days

(Me$_3$Si)$_2$CH-C(Me$_3$Si)$_2$ >110 days

Combined steric and electronic effects

Galvinoxyl and diphenylpicrylhydrazyl (DPPH) are comertially available radicals

Carbocations

Sensitive to the media (more than radicals!). Different chemistries in the gas and condensed phases.

Thermodynamic stability in the gas phase is estimated by hydride ion affinity , HIA

$$RH \rightarrow R^+ + H^-$$

HIA is a heterolytic analog of BDE. A larger HIA implies less stable carbocation

HIA, kcal/mol

CH_3^+	312
$C_2H_5^+$	273
$CH_3CH_2CH_2^+$	266
$Ph\text{-}CH_2^+$	234

$3^0 > 2^0 > 1^0 >$ methyl

$\longleftarrow$

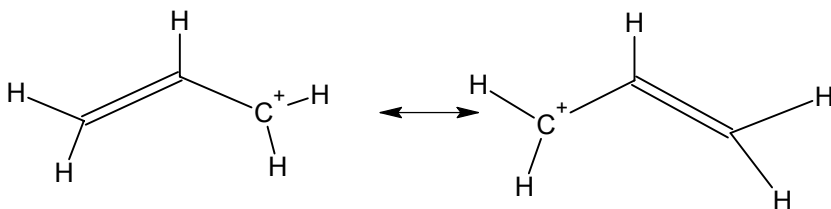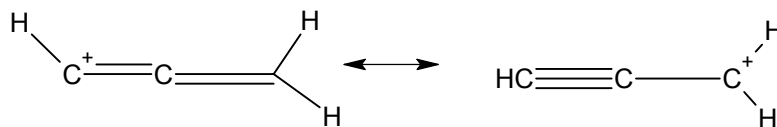stability

$$sp > sp^2 > sp^3$$

⟵ electronegativity

stability ⟶

Compare allyl and propargyl

HIA of allyl cation is 258 kcal/mol

HIA of propargyl cation is 270 kcal/mol

Resonance effect with sp is less efficient than with sp^2 carbon

Heteroatom effects

π- and σ- donors stabilize carbocations. Acceptors (electronegative elements) destabilize

F- weak π- donor and strong σ- acceptor. Total effect- destabilization, if compare with $X-CH_2^+$

NH_2- good π-donor, stabilizing effect; OH- less so as it is more electronegative than N

HIA, kcal/mol

CH_3^+	312
$NH_2CH_2^+$	218
$HO-CH_2^+$	243
$F-CH_2^+$	290
$NC-CH_2^+$	318

Electron withdrawing groups such as NC greatly destabilize cations

Geometries- prefer to be planar at the cationic center

Stable Ion Media   Olah-Nobel Prize in 1994

The most common rxn of carbocations- nucleophilic attack

The media must a VERY poor nucleophile (Lewis super- acid)

SbF_5^- antimony pentafluoride

$$RX + SbF_5 \rightarrow R^+ + Sb_2F_{10}X^-$$

In fact, we are not making carbocation more stable but more persistent!

Lifetimes of carbocations- need stable ion media to persist for more than 10^{-9} s