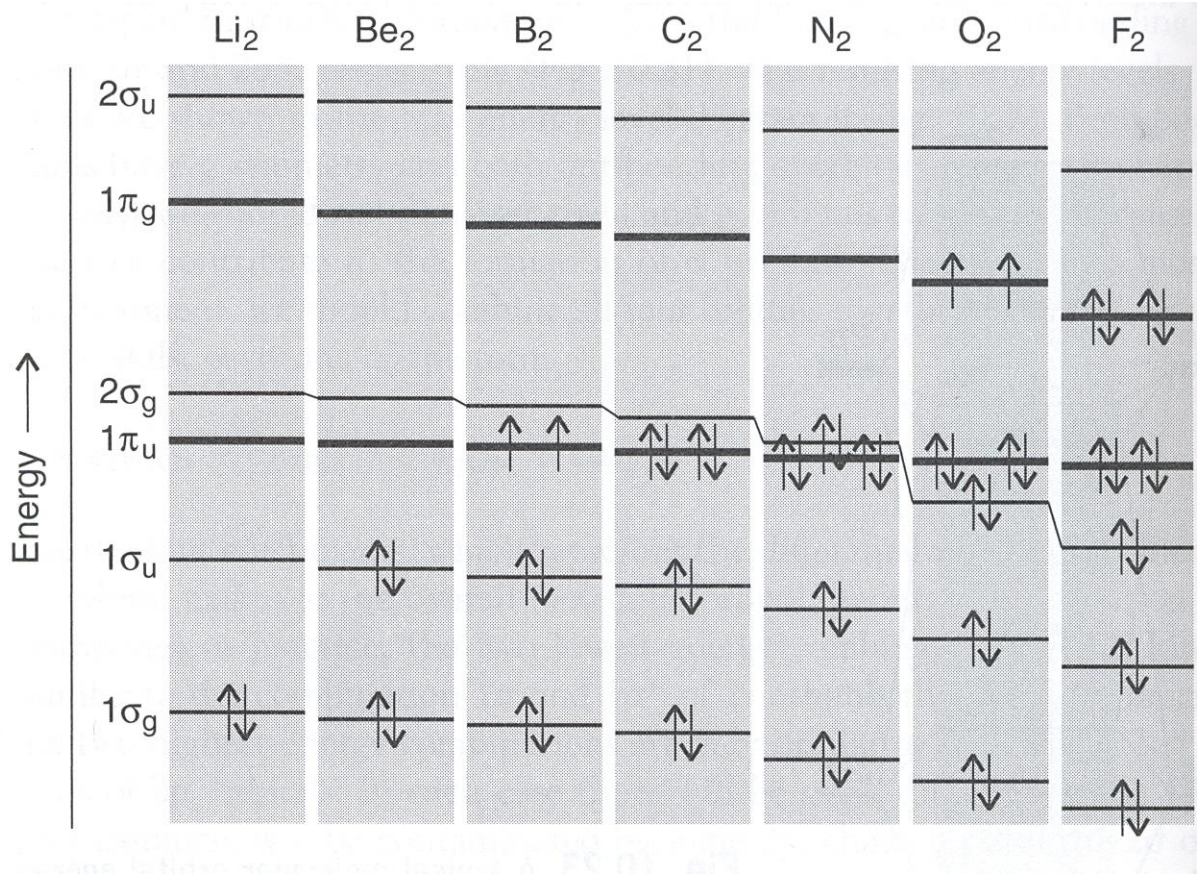
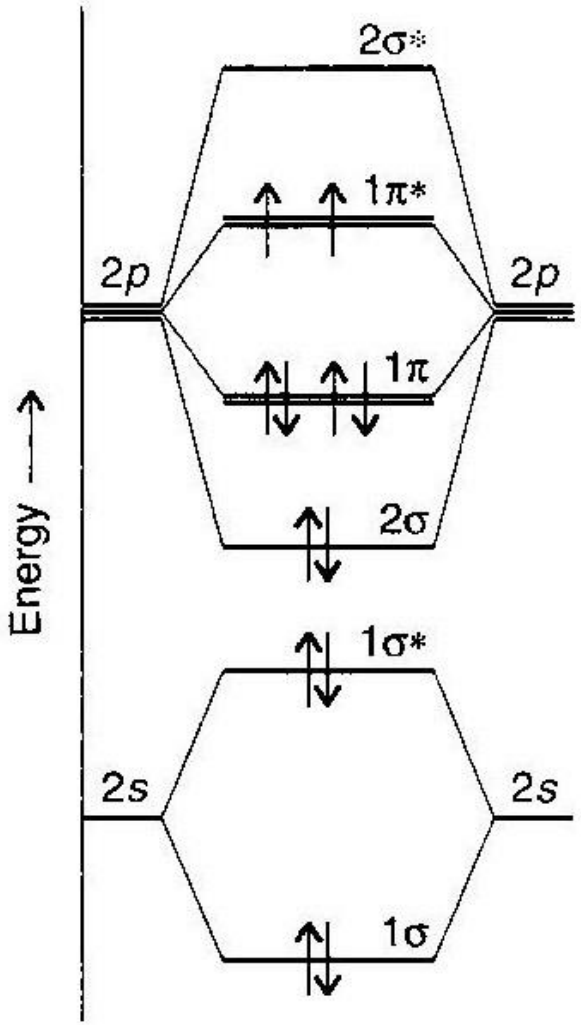
Gyökös reakciók

The structure of O_2 cannot be adequately explained by line-bond formulas because two 2*p* electrons are in antiboinding orbitals. Molecular oxygen will represented as ·O-O· or simply O_2. $E_{O\text{-}O}<E_{O2}$

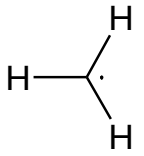
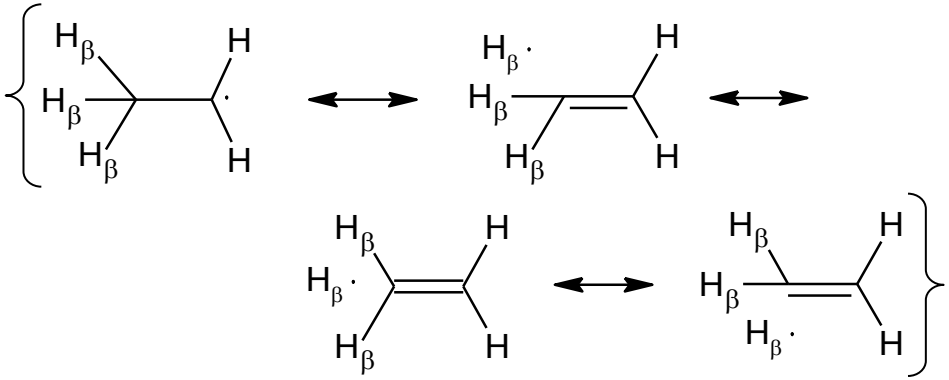
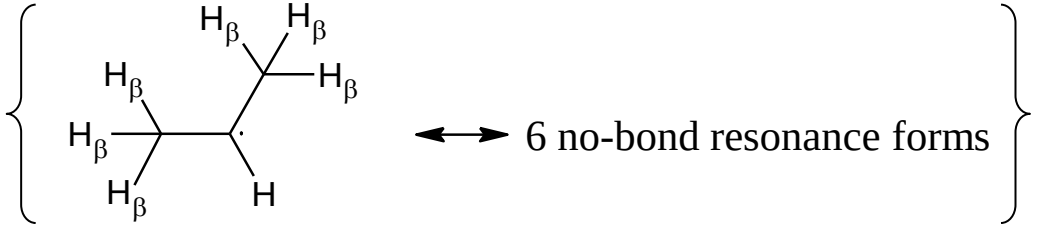
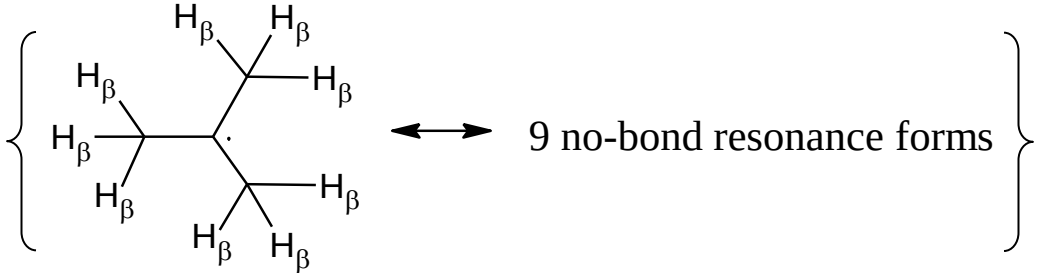


The variation of the orbital energies of Period 2 homonuclear diatomic molecules. Only the valence shell orbitals are shown.

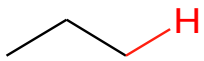
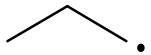
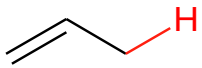
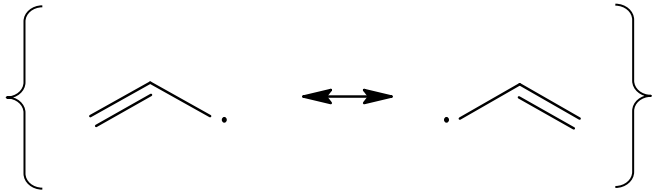
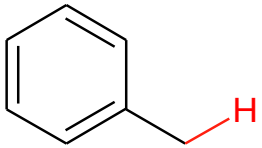
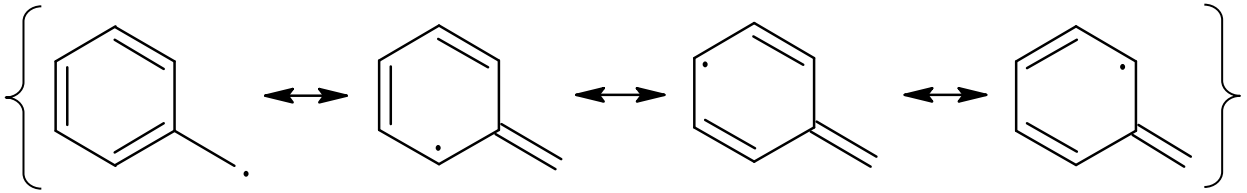


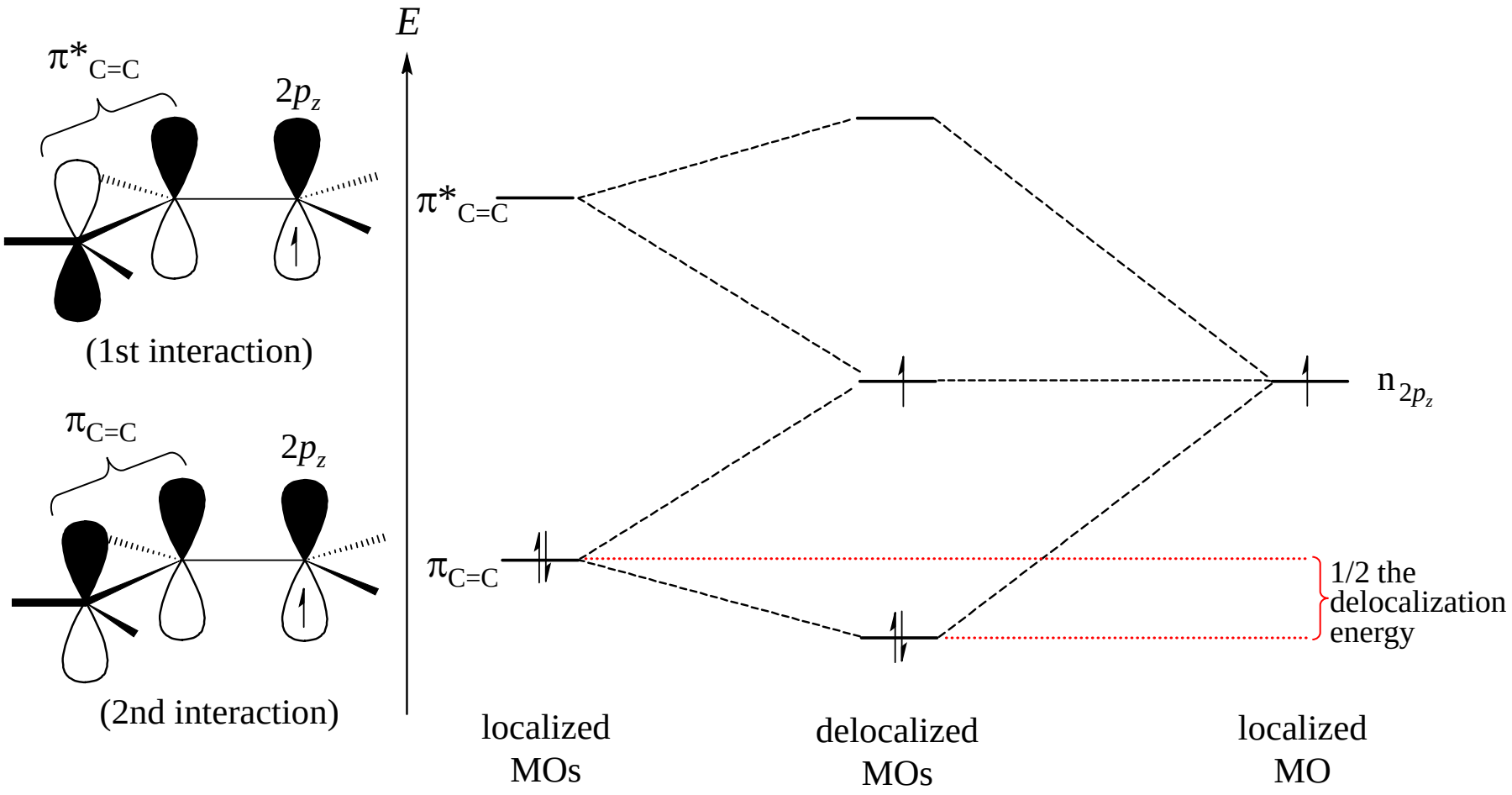
A typical molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules. The valence atomic orbitals are drawn in the columns on the left and the right; the molecular orbitals are shown in the middle. Note that the π orbitals form doubly degenerate pairs. The sloping lines joining the molecular orbitals to the atomic orbitals show the principal composition of the molecular orbitals. This diagram is suitable for O_2 and F_2; the configuration of O_2 is shown.

Stabilization of radicals by alkyl substituents

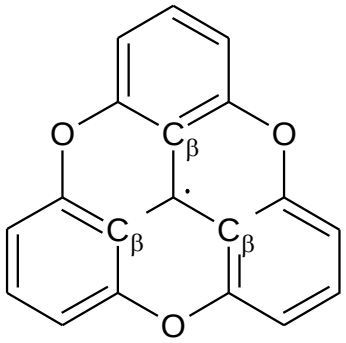
	DE **kcal/mol**	**VB formulation of the radical R•**
$H_3C—H$	104	
$H_3C—H_2C—H$	98	 i.e., 1 no-bond resonance form per H_β
$(H_3C)_2HC—H$	95	 6 no-bond resonance forms
$(H_3C)_3C—H$	92	 9 no-bond resonance forms

Stabilization of radicals by unsaturated substituents

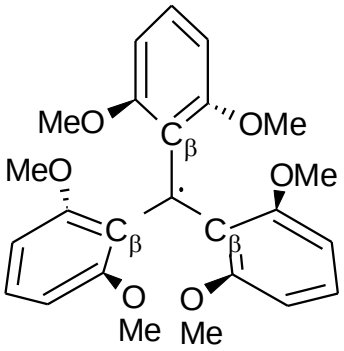
	DE **kcal/mol**	**VB formulation of the radical R•**
	98	
	89	
	89	



Stabilization by overlap of a singly occupied $2p_z$ AO with adjacent parallel $\pi_{C=C}$- or $\pi^*_{C=C}$- MOs.

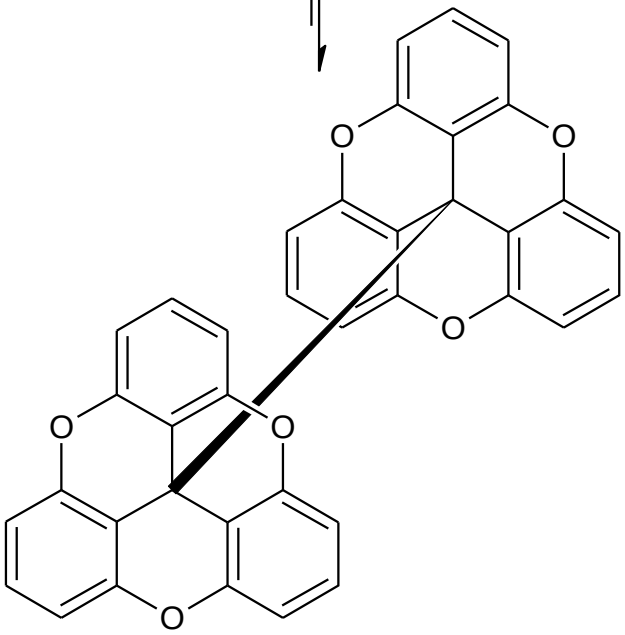


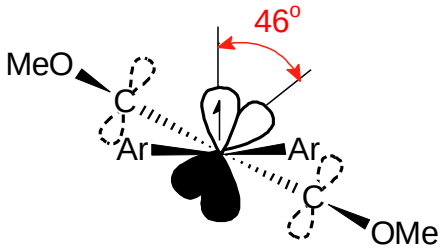
A



B

is

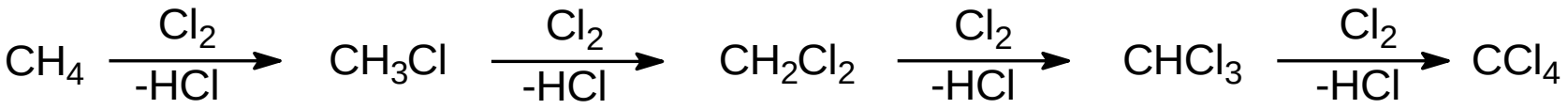




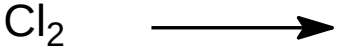
Dimer

Comparison of the trityl radical derivatives A and B; A dimerizes, B does not.

Gyökös halogénezés lépései

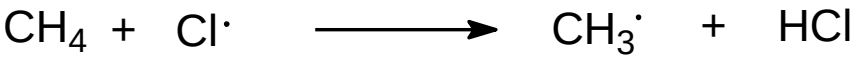


Láncindító reakció

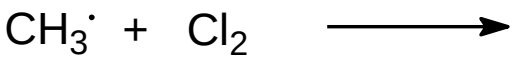


243 kJ mol^{-1}

Láncvivő reakció



3 kJ mol^{-1}

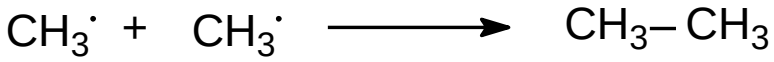


-108 kJ mol^{-1}

Láncletörő reakció

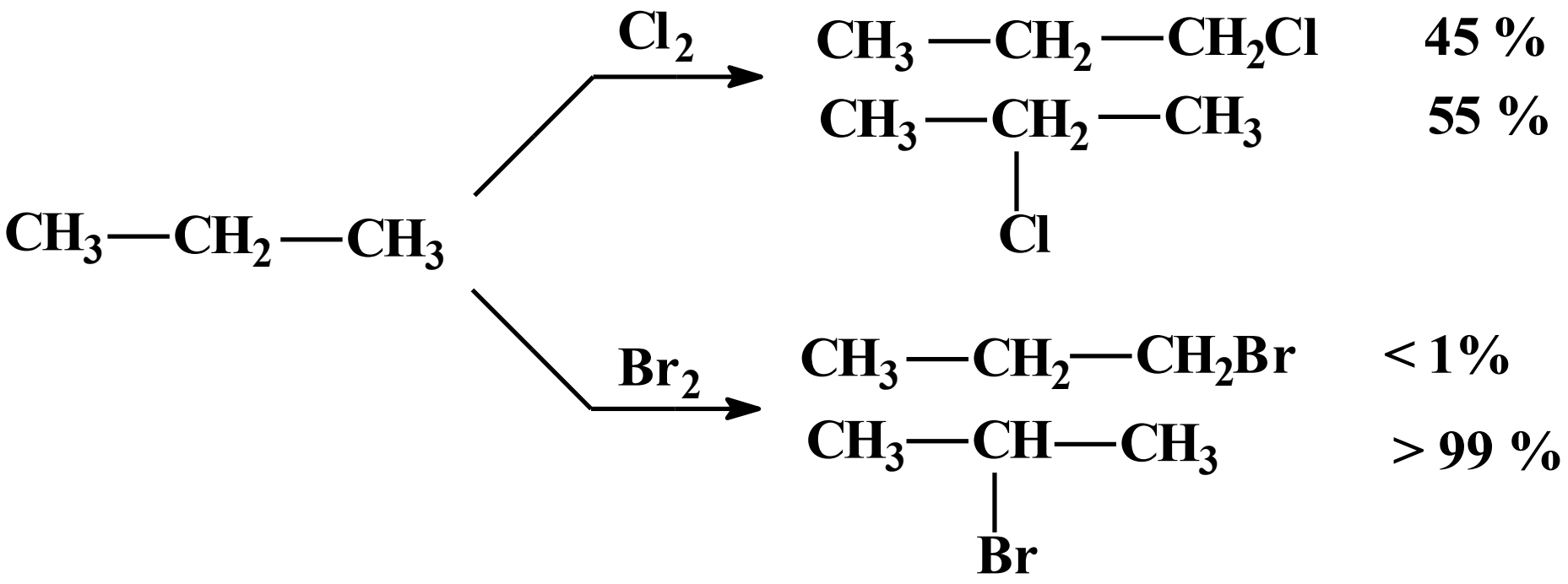
350 kJ mol^{-1}

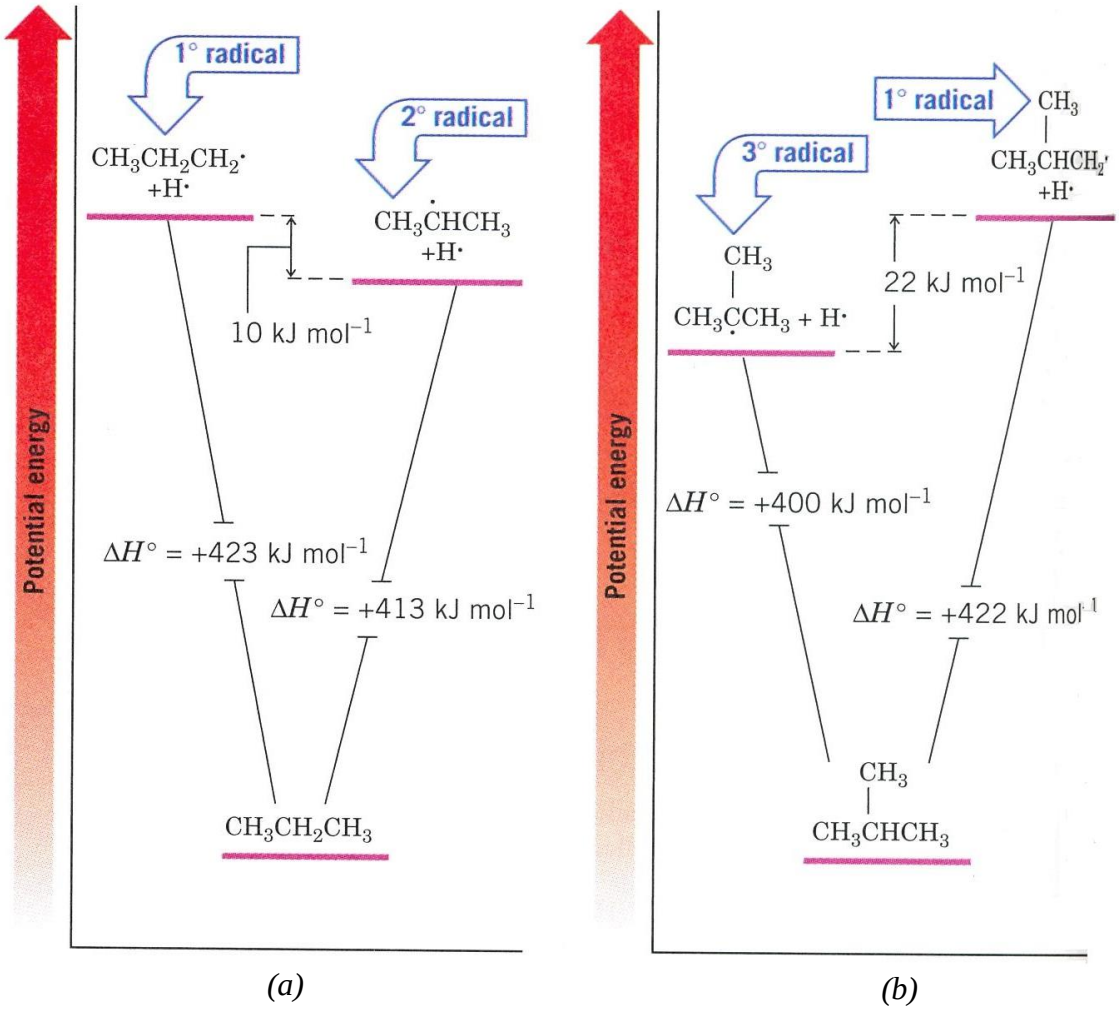
-243 kJ mol^{-1}



-369 kJ mol^{-1}

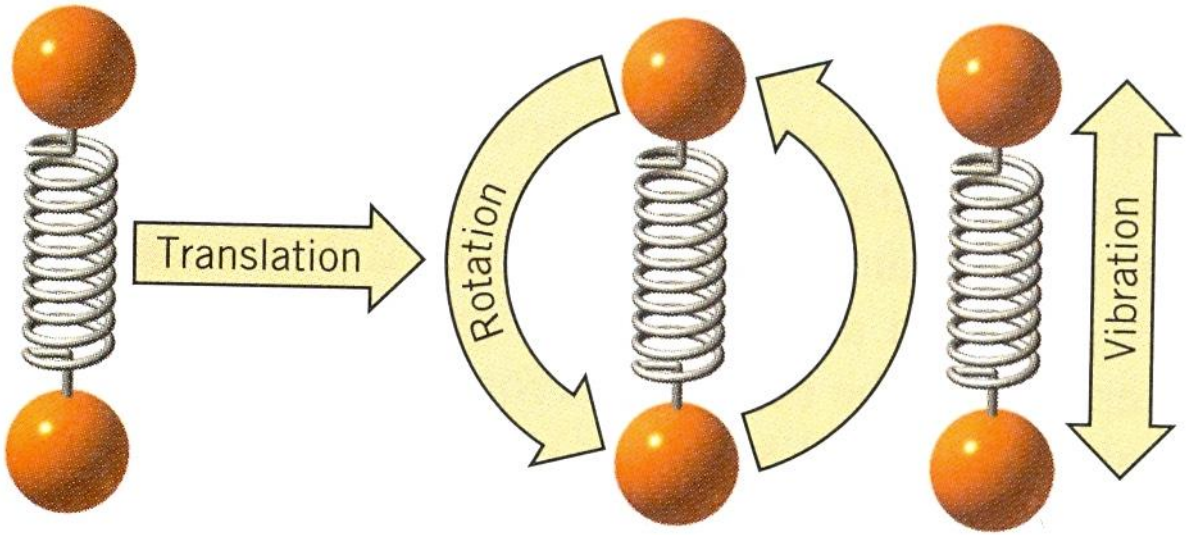
Reaktivitás – szelektivitás szabálya



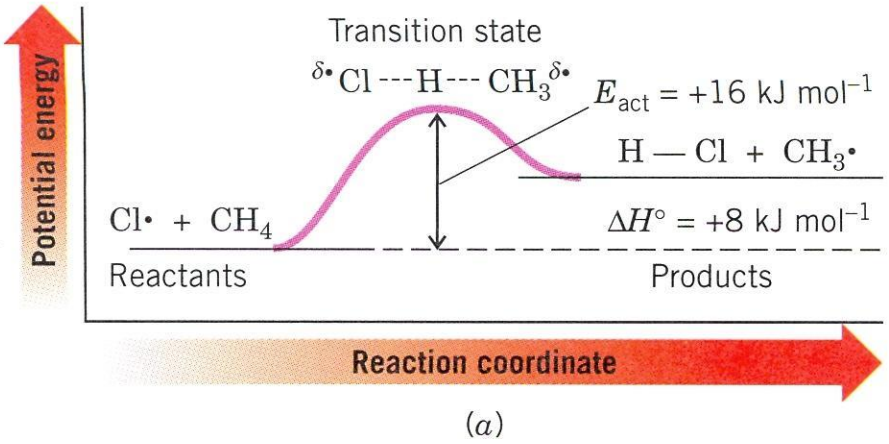


(*a*) Comparison of the potential energies of the propyl radical (+H•) and the isopropyl radical (+H•) relative to propane. The isopropyl radical (a 2° radical) is more stable than the 1° radical by 10kJ mol^{-1}.

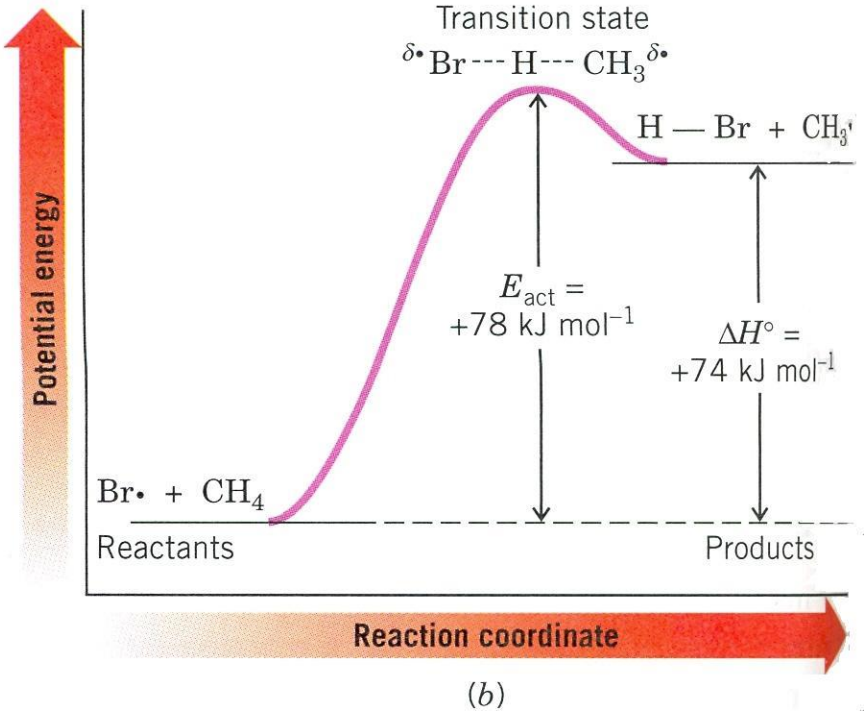
(*b*) Comparisonof the potential energies of the *tert*-butyl radical (+H•) and the isobutyl radical (+H•) relative to isobutane. The 3° radical is more stable than the 1°radical by 22 kJ mol^{-1}.



Translational, rotational and vibrational degrees of freedom for a simple diatomic molecule.

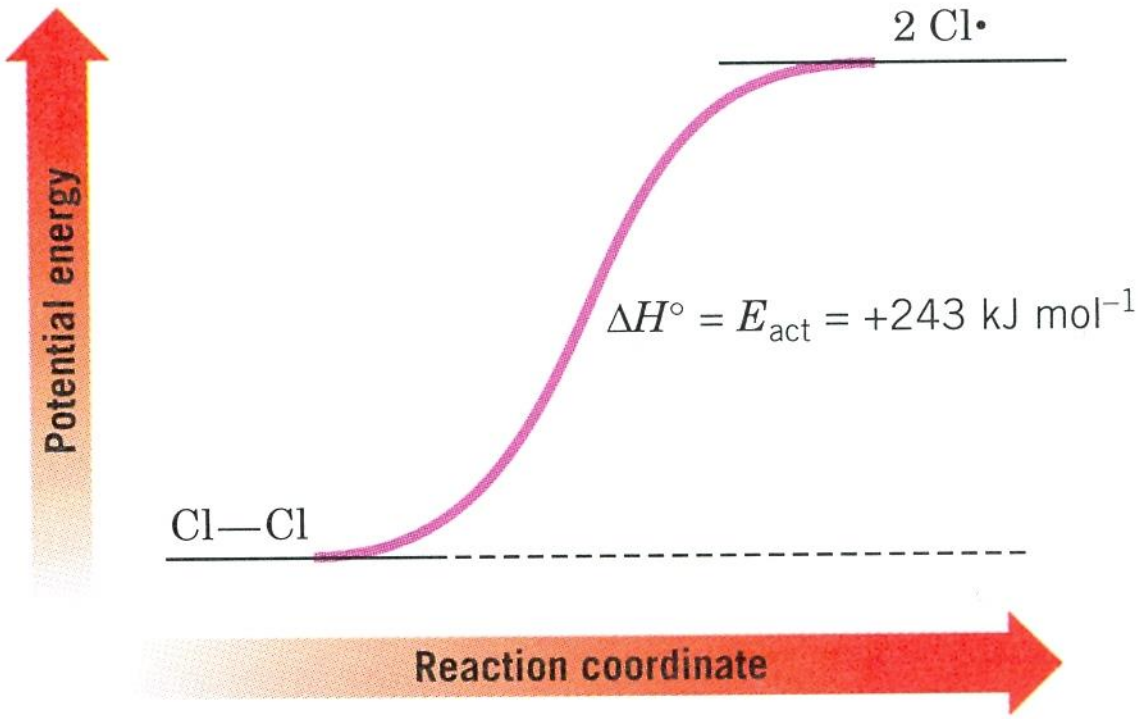


(a)

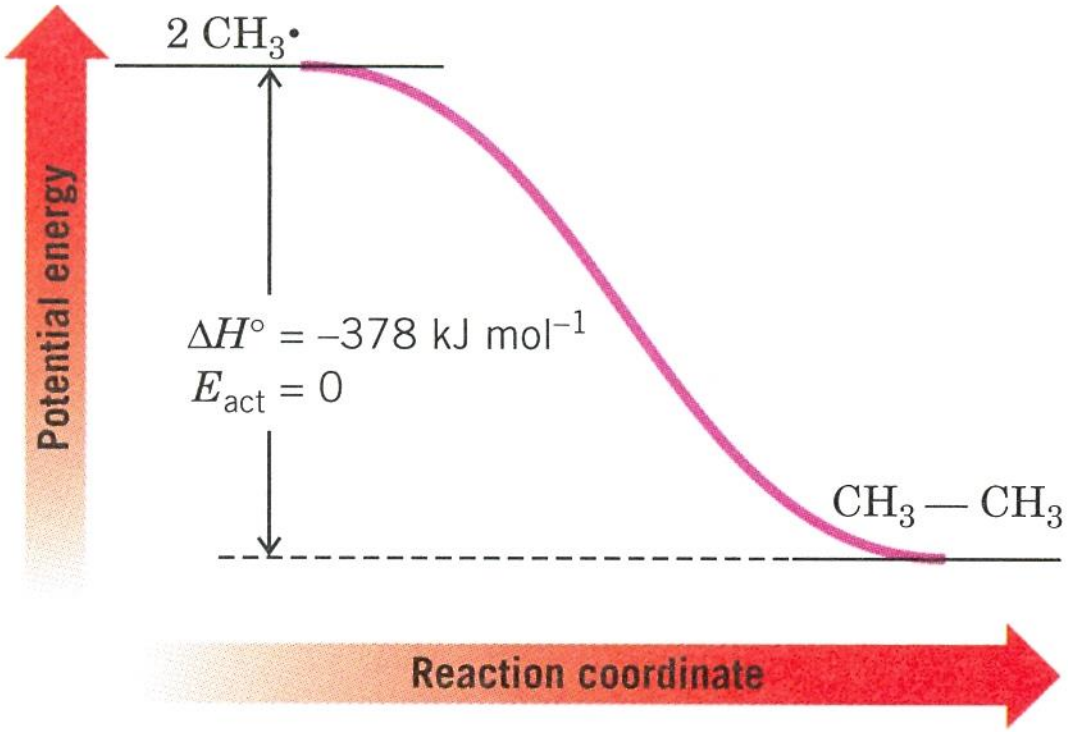


(b)

Potential energy diagrams for (a) the reaction of a chlorine atom with methane and (b) the reaction of a bromine atom with methane.

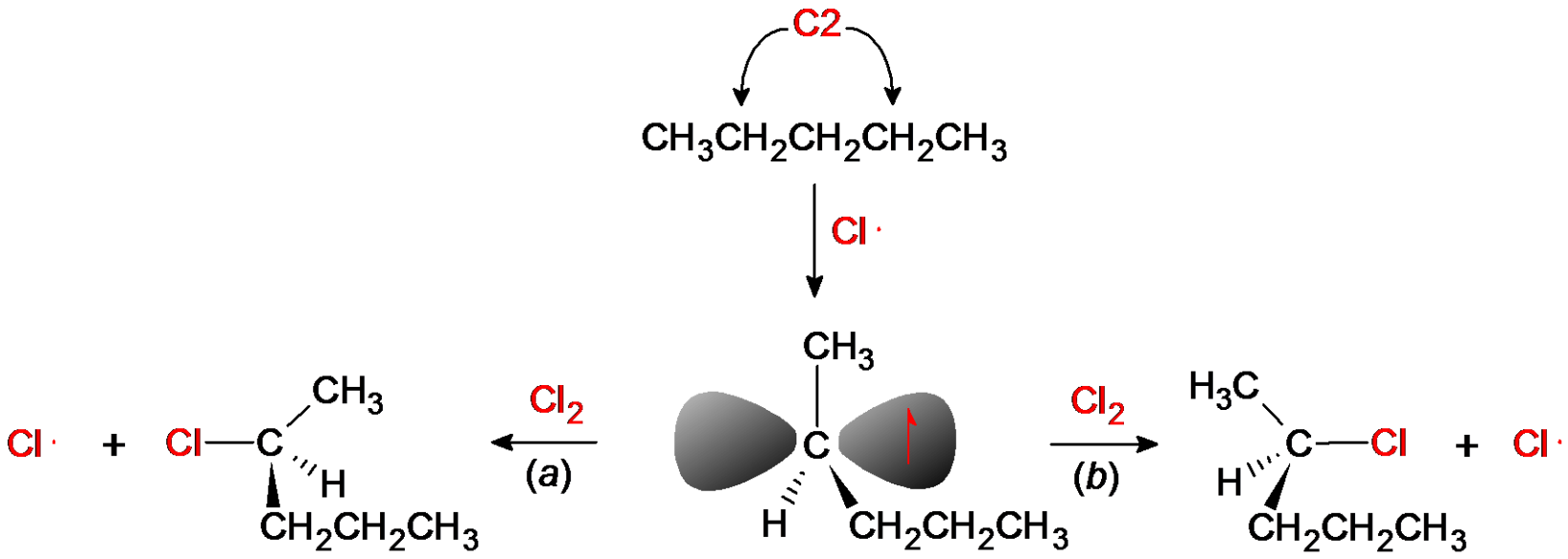


Potential energy diagram for the dissociation of a chlorine molecule into chlorine atoms.



Potential energy diagram for the combination of two methyl radicals to form a molecule of ethane.

The stereochemistry of chlorination at C2 of pentane

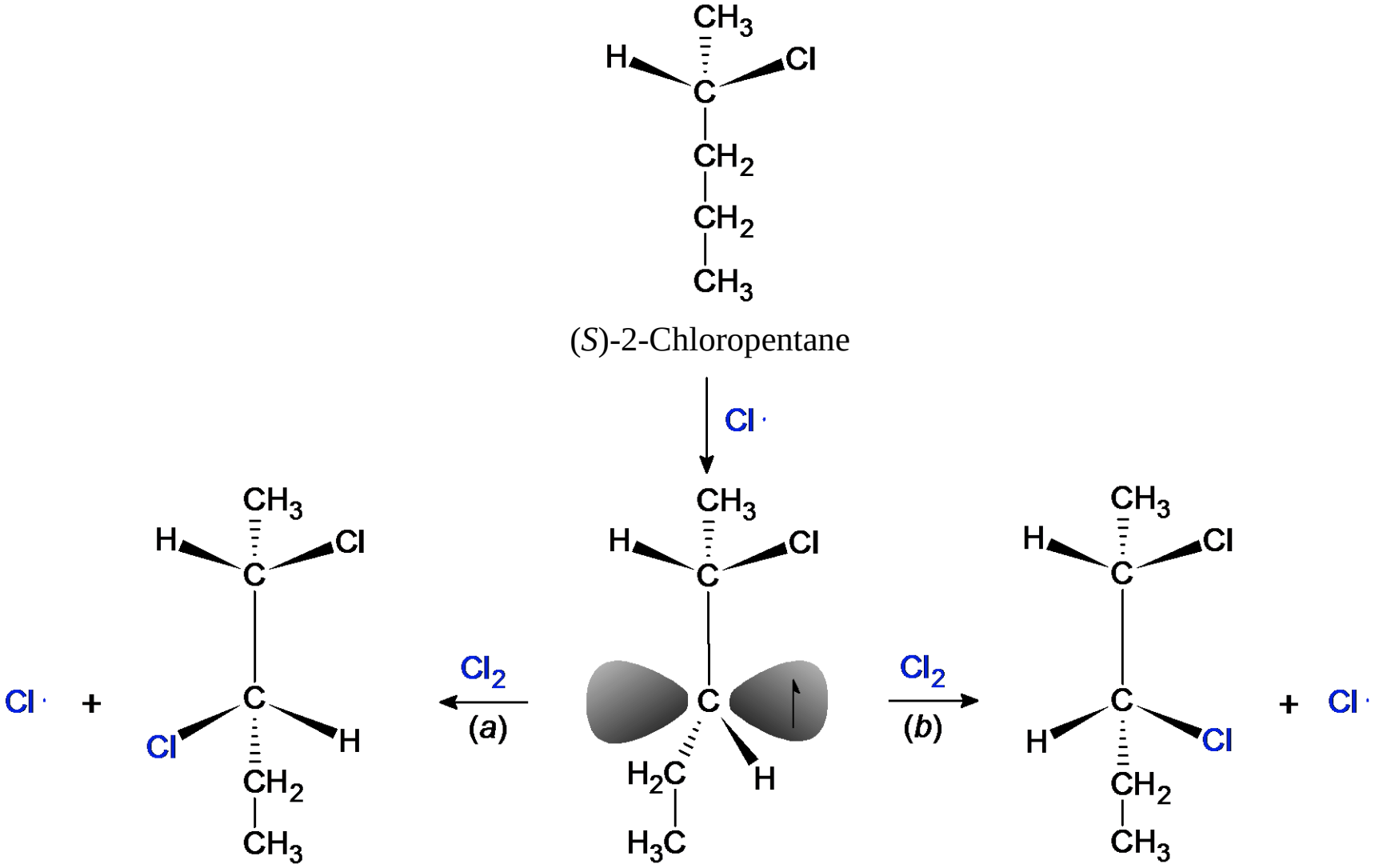


(*S*)-2-Chloropentane
(50 %)

Trigonal planar
radical
(achiral)

(*R*)-2-Chloropentane
(50 %)

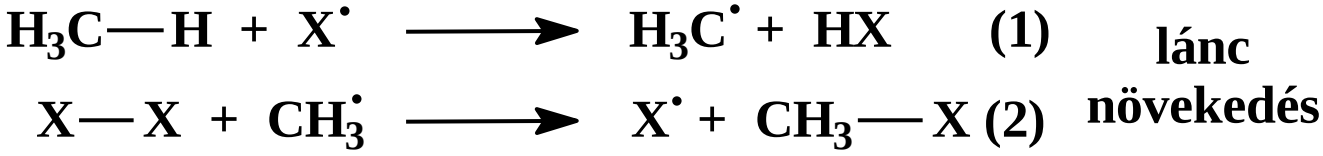
The stereochemistry of chlorination at C3 of (*S*)-2-chloropentane



Gyökös reakciók
Termokémia I.

ΔH reakció = -KDE (termékek) - [-KDE (reaktánsok)]

Metán halogénezése



		KDE (kcal/mol)
F—F	→ 2 F•	38
Cl—Cl	→ 2 Cl•	58
Br—Br	→ 2 Br•	46
I—I	→ 2 I•	36
H—F	→ H• + F•	136
H—Cl	→ H• + Cl•	103
H—Br	→ H• + Br•	87
H—I	→ H• + I•	71

Gyökös reakciók
Termokémia II.

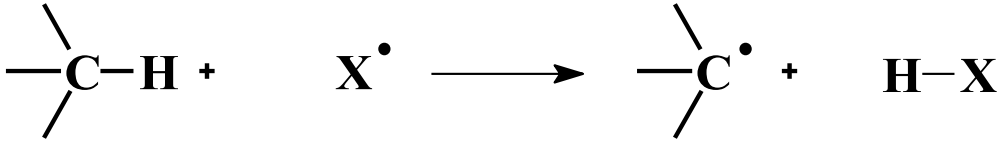
R—H	KDE (kcal/mol)
H_3C—H	104
1° C —H	98
2° C —H	94
3° C —H	91
H_3C —F	108
H_3C —Cl	83
H_3C —Br	70
H_3C —I	56

Gyökös reakciók
Termokémia III.

KDE (kcal/mol)	104	58	2 * 103
	162		206

ΔH_r = - 206 - (-162) = - 44 kcal/mol

A halogénezési láncnövekedés (1) lépése:



kötés	X = Cl	ΔH_r	X = Br
H_3C—H	-103-(-104) = +1		-87-(-104) = +17
3° C—H	-103-(-91) = -12		-87-(-91) = +4

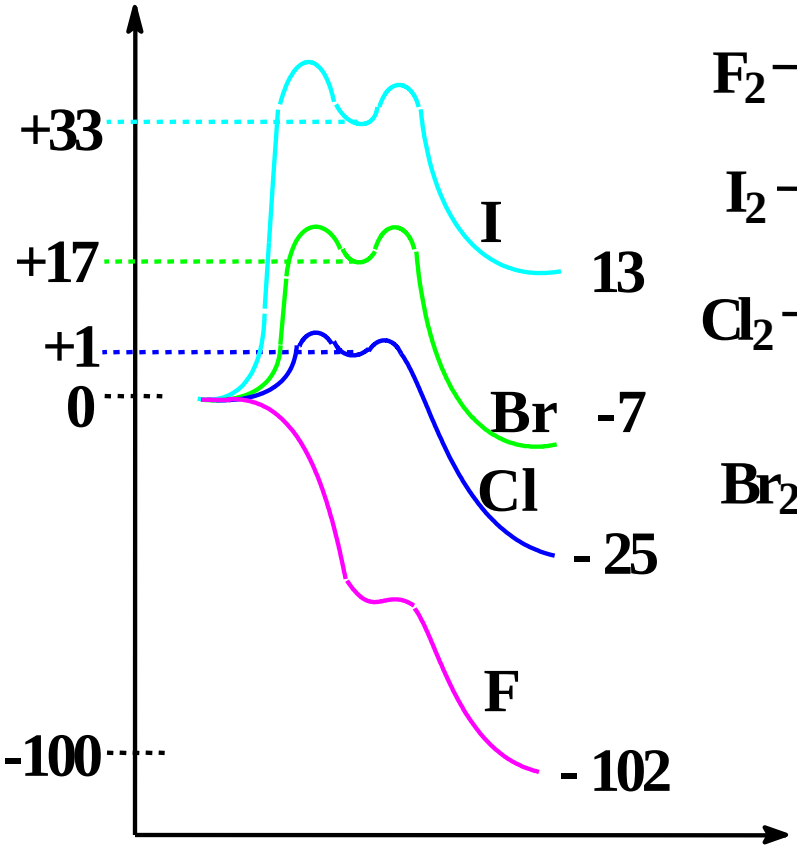
Vagyis: a lánc növekedés első lépése endoterm, (de a teljes, (1) és (2) exoterm)
Br sokkal jobban válogat 1°-ot nem!

Gyökös reakciók
Termokémia IV.

$$X{-}X + CH_3^{\bullet} \longrightarrow H_3C{-}X + X^{\bullet} \qquad (2)$$

$$CH_4 + X^{\bullet} \longrightarrow CH_3^{\bullet} + HX \qquad (1)$$

A halogénezés láncnövekedési lépéseinek energiaprofilja:



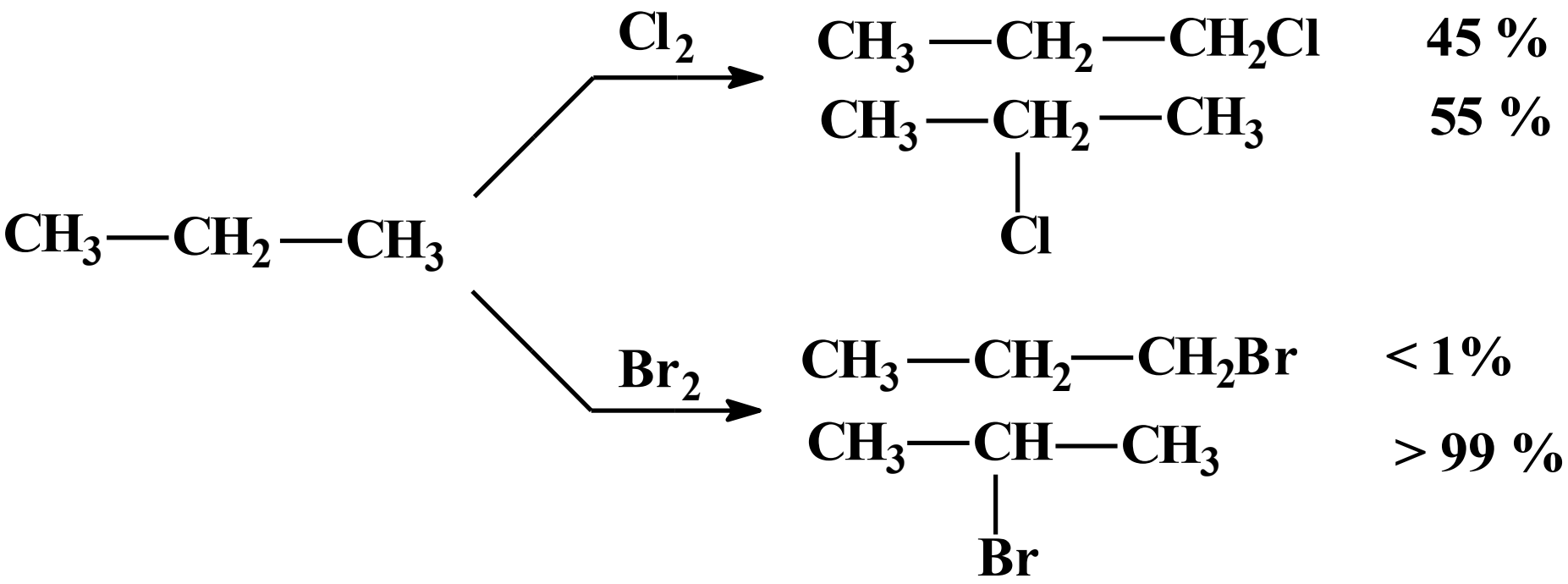
F_2 → extrém reaktív → robbanás

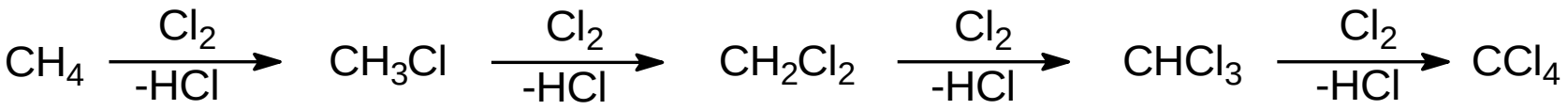
I_2 → endoterm → nem megy

Cl_2 → reaktivitása nagy → nem szelektív

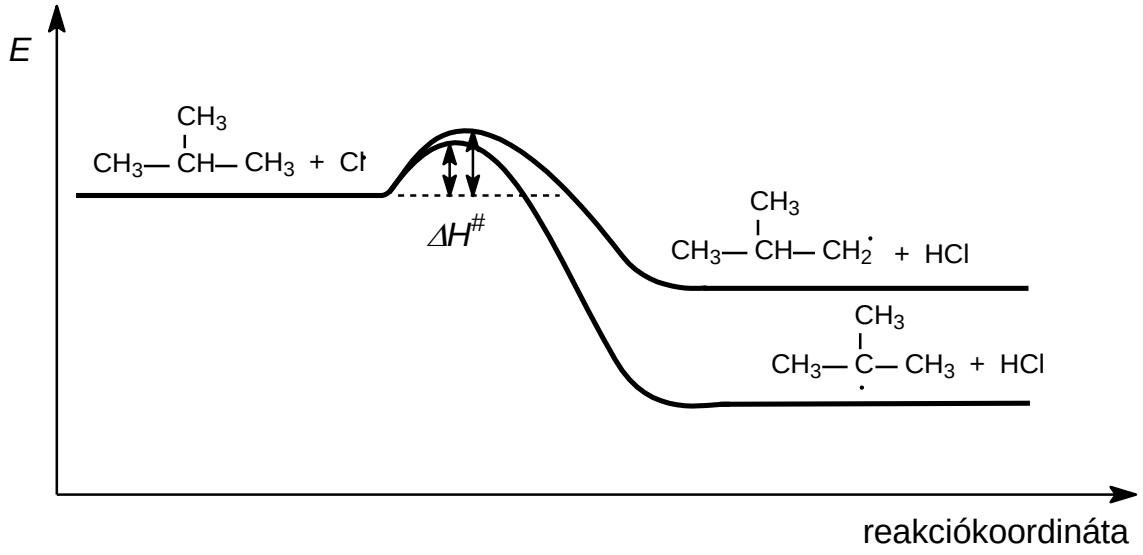
Br_2 → lomha → szelektív (csak a reaktívat)

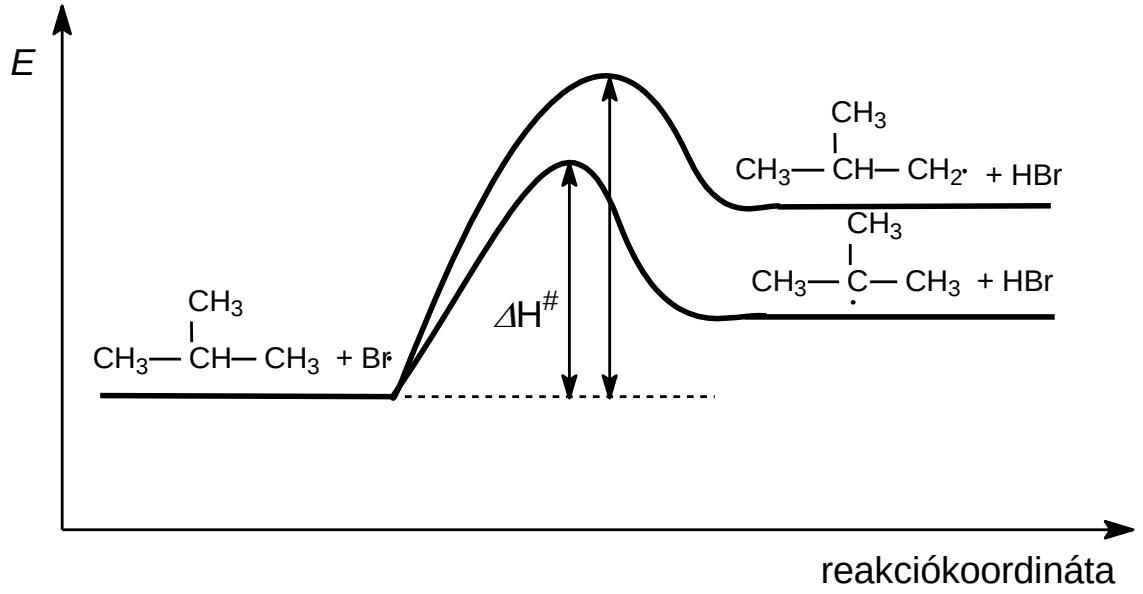
Gyökös reakciók
Termokémia V.



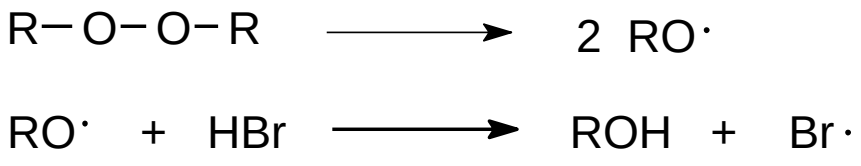


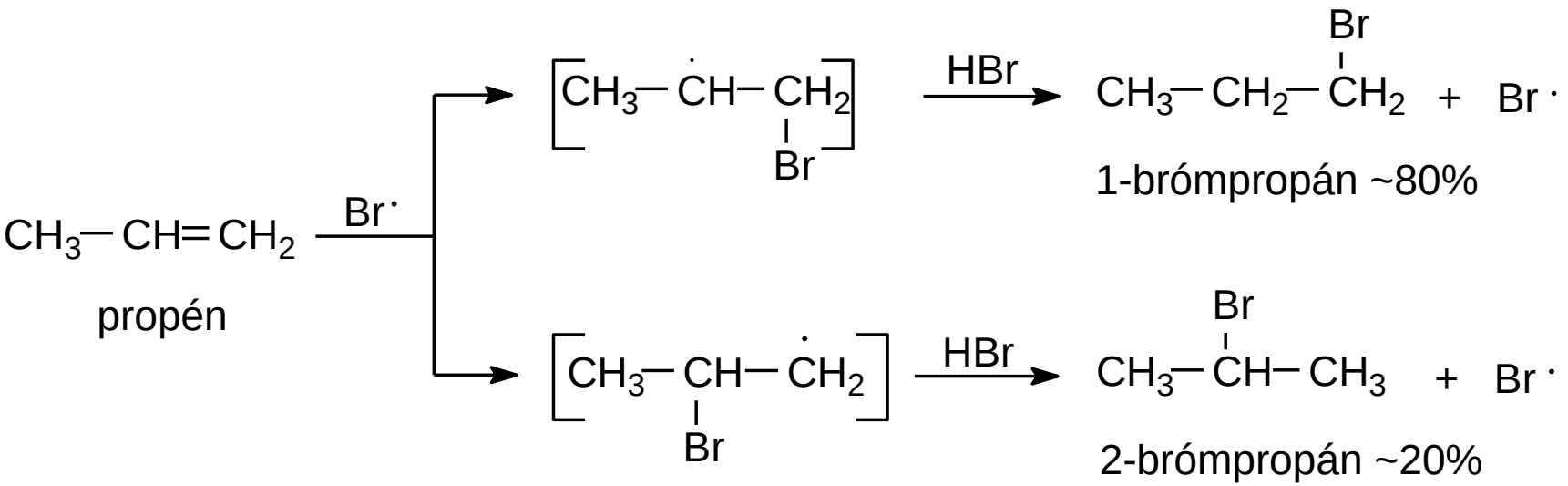
Láncindító reakció	$Cl_2 \longrightarrow 2Cl^{\cdot}$		243 kJ mol^{-1}
Láncvivő reakció	$CH_4 + Cl^{\cdot} \longrightarrow CH_3^{\cdot} + HCl$		3 kJ mol^{-1}
	$CH_3^{\cdot} + Cl_2 \longrightarrow CH_3Cl + Cl^{\cdot}$		-108 kJ mol^{-1}
Láncletörő reakció	$CH_3^{\cdot} + Cl^{\cdot} \longrightarrow CH_3Cl$		350 kJ mol^{-1}
	$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$		-243 kJ mol^{-1}
	$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow CH_3–CH_3$		-369 kJ mol^{-1}

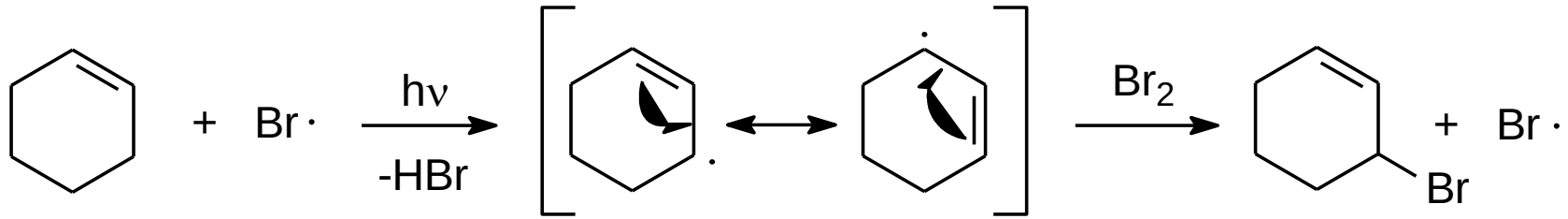

E
CH3
CH3— CH— CH3 + Cl
ΔH#
CH3
CH3— CH— CH2 + HCl
CH3
CH3— C— CH3 + HCl
reakciókoordináta


E
CH3
CH3— CH— CH2 + HBr
CH3
CH3— C— CH3 + HBr
CH3
CH3— CH— CH3 + Br
ΔH#
reakciókoordináta

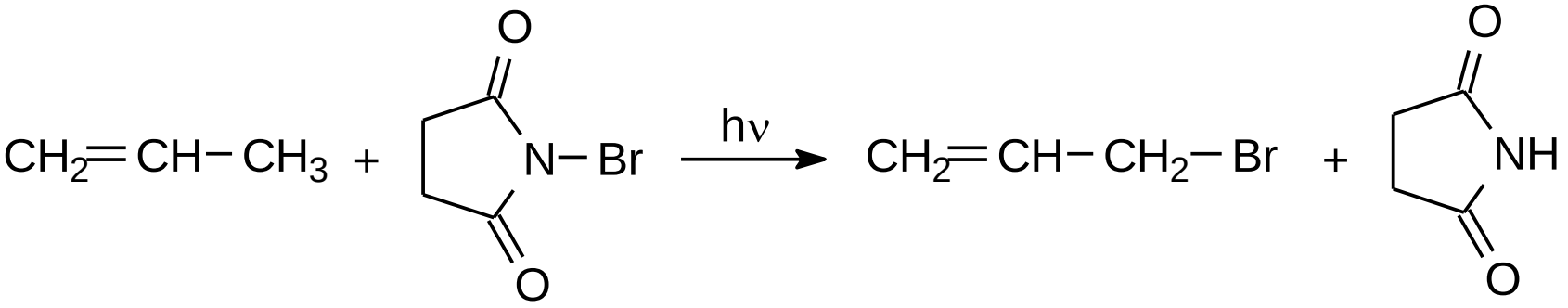
brómgyök képződés:





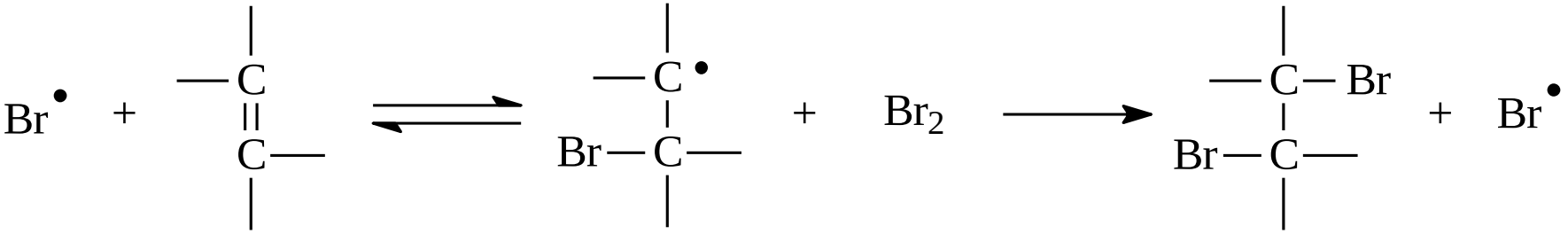


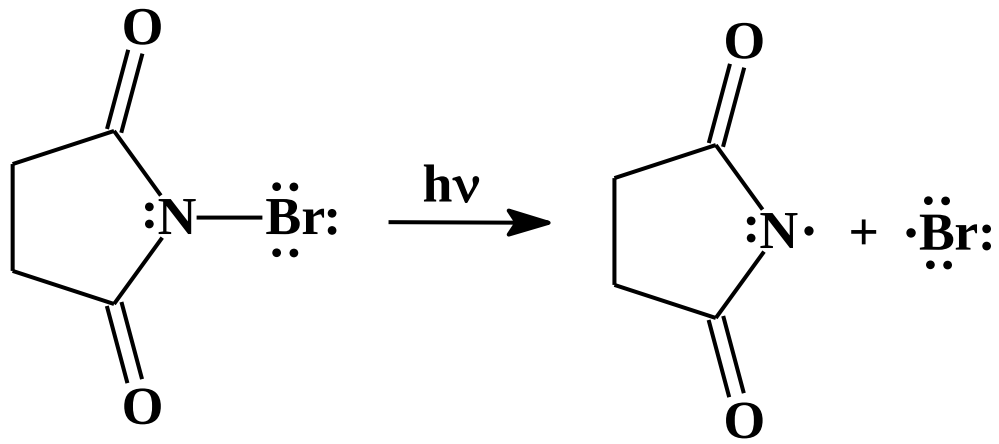
ciklohexén allil-típusú gyök 3-brómciklohexén

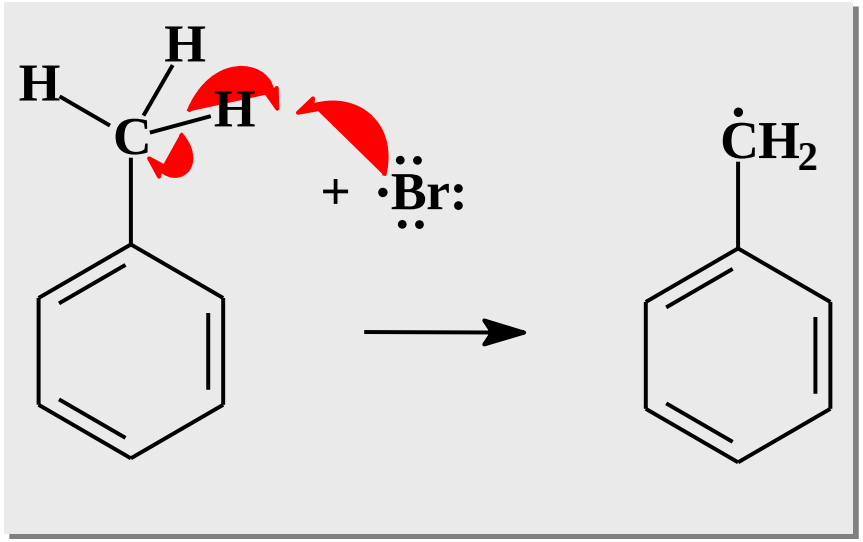


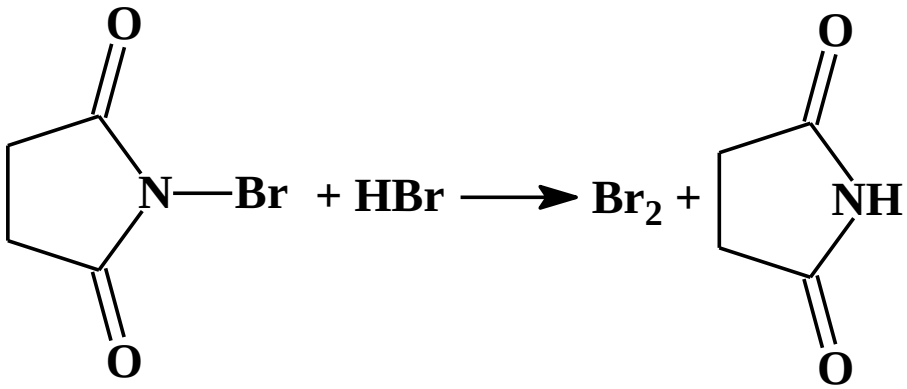
propén N-brómszukcinimid allil-bromid szukcinimid

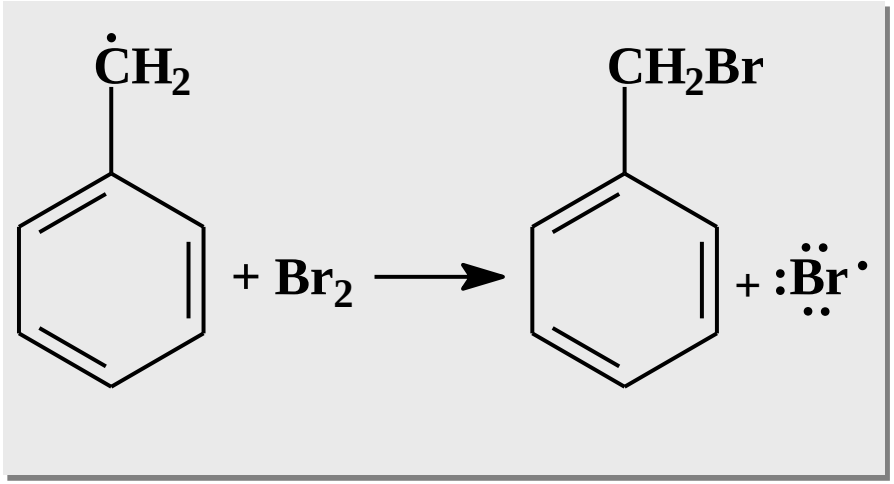
Alacsony Br_2 koncentráció esetén (*N*-brómszukcinimid esetén) az addíció háttérbe szorul, az addíciós termék könnyen visszaalakul a kiindulási olefinné. Magasabb Br_2 koncentrációnál az addíciós reakció kerül előtérbe – az elsőként támadó bróm-gyök reakcióját követően a második bróm-gyök egy másik bróm-molekulából származik, amelyhez viszont magasabb brómkoncentráció szükséges.











Alacsony Br_2 koncentráció