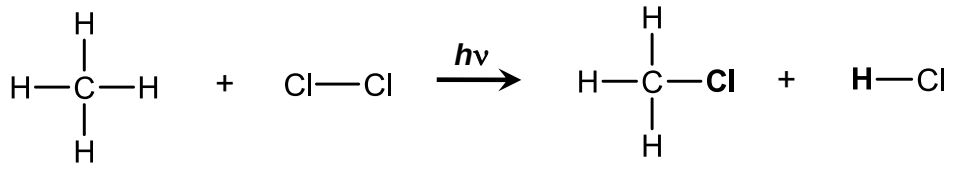
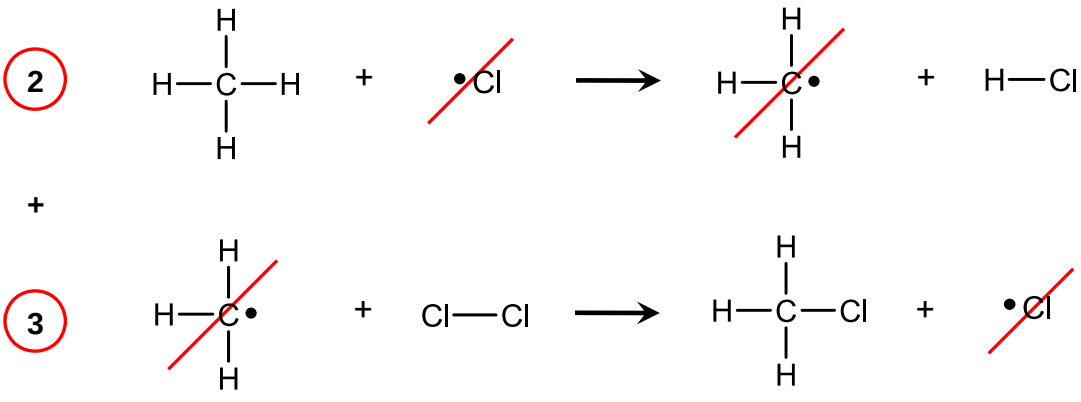
Alkane Halogenation via Free-Radical Chain Reaction

Free-radical halogenation converts C_{sp^3}-H into C-Cl or C-Br.



Free-radical chain reaction mechanism defined by *initiation*, *propagation* and *termination* steps.

Overall Chain Reaction Described by Sum of Propagation Steps

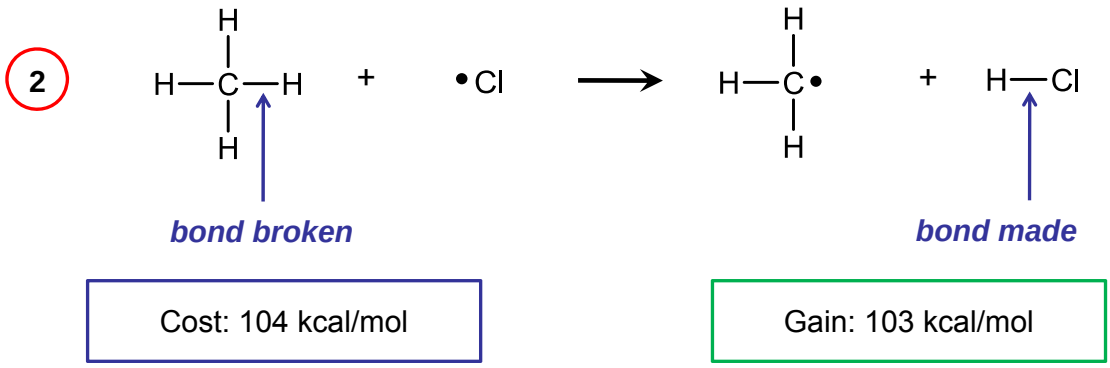


Bond Dissociation Enthalpies

BDE: Enthalpy required to break a bond into component radicals (A—B → A• + •B)

Bond	BDE (kcal/mol)	Bond	BDE (kcal/mol)
Cl—Cl	**58**	**CH_3—Cl**	**84**
H—Cl	**103**	CH_3CH_2—Cl	81
		$(CH_3)_2CH$—Cl	80
CH_3—H	**104**	$(CH_3)_3C$—Cl	79
CH_3CH_2—H	98		
$(CH_3)_2CH$—H	95	CH_3—Br	70
$(CH_3)_3C$—H	91	CH_3CH_2—Br	68
$C_6H_5CH_2$—H	88	$(CH_3)_2CH$—Br	68
CH_2=CH-CH_2—H	86	$(CH_3)_3C$—Br	65

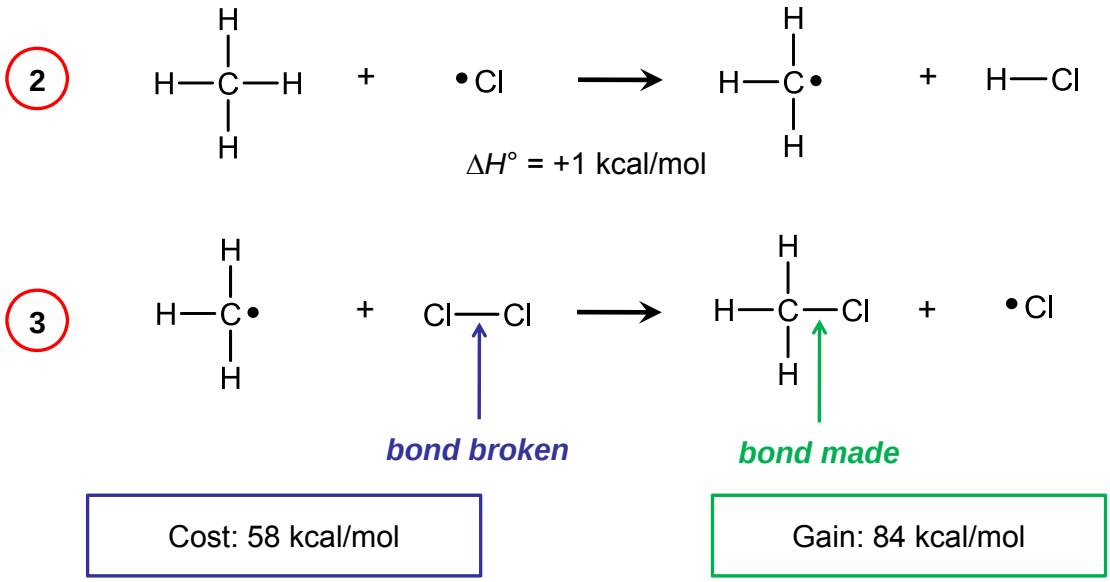
Halogenation Steps Involve Bond Making & Bond Breaking



$\Delta H°$ for this step: +1 kcal/mol

Important note: This analysis works only for homolytic (radical-producing) steps. Can't use to describe ions, so can't use to calculate $\Delta H°$ for S_N1 steps.

Thermodynamics of Propagating Halogenation



$\Delta H°$ for this step: -26 kcal/mol

Thermodynamics of Propagating Halogenation