radical halogenation of alkanes

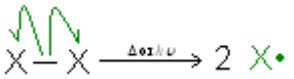
reaction type: radical substitution

reaction:

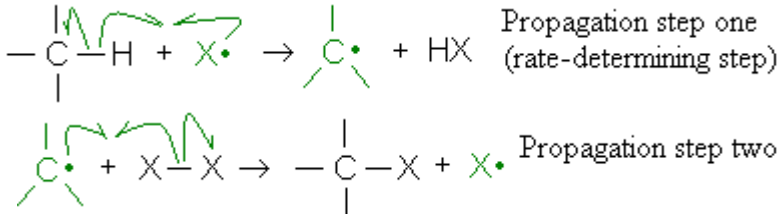
X = F, Br, or Cl

mechanism: (radical chain)

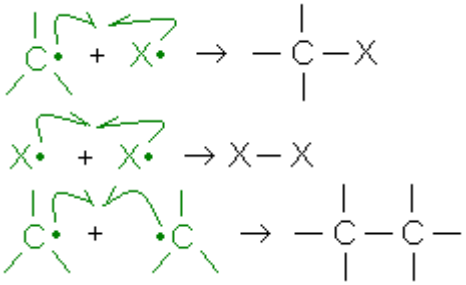
initiation (nonradical → 2 radicals):



propagation (radical + nonradical → radical + nonradical):



termination (2 radicals → nonradical):



regiochemistry:

For fluorine, which is highly reactive and thus unselective, “statistics” dominates, and the major product usually comes from abstracting the type of hydrogen in greatest abundance.

For bromine, which is less reactive and thus more selective, “electronics” dominates; the major product comes from abstracting the hydrogens on the most substituted carbon.

For chlorine, with intermediate reactivity and selectivity, the major product is calculated using chlorine’s selectivity ratio (3°:2°:1° = 5:4:1) and the statistical ratio of the hydrogens.

stereochemistry: maximum of two stereoisomers, in equal amounts
(because the carbon-radical intermediate is trigonal planar)

synthetic usefulness: Radical halogenation is useful for introducing a functional group into a non-functionalized molecule.

Bromination is most useful for synthesis because it is highly selective for the hydrogens on the most substituted carbon. Because chlorine and fluorine are less selective, they tend to give a mix of products and thus are less useful for synthesis.