13.5: Chlorination of Other Alkanes

When alkanes larger than ethane are halogenated, isomeric products are formed. Thus chlorination of propane gives both 1-chloropropane and 2-chloropropane as mono-chlorinated products. Four constitutionally isomeric dichlorinated products are possible, and **five constitutional isomers** exist for the trichlorinated propanes. Can you write structural formulas for the four dichlorinated isomers?

$$CH_3CH_2CH_3 + 2Cl_2 \rightarrow \text{Four } C_3H_6Cl_2 \text{ isomers} + 2HCl \tag{13.5.1}$$

The halogenation of propane discloses an interesting feature of these reactions. **All the hydrogens in a complex alkane do not exhibit equal reactivity**. For example, propane has eight hydrogens, six of them being structurally equivalent **primary**, and the other two being **secondary**. If all these hydrogen atoms were equally reactive, halogenation should give a 3:1 ratio of 1-halopropane to 2-halopropane mono-halogenated products, reflecting the primary/secondary numbers. This is not what we observe. Light-induced gas phase chlorination at 25 ºC gives 45% 1-chloropropane and 55% 2-chloropropane.

CH_3-CH_2-CH_3 + Cl_2 → 45% CH_3-CH_2-CH_2Cl + 55% CH_3-$CHCl$-CH_3

The results of bromination (light-induced at 25 ºC) are even more suprising, with 2-bromopropane accounting for 97% of the mono-bromo product.

CH_3-CH_2-CH_3 + Br_2 → 3% CH_3-CH_2-CH_2Br + 97% CH_3-$CHBr$-CH_3

These results suggest strongly that 2º-hydrogens are inherently more reactive than 1º-hydrogens, by a factor of about 3:1. Further experiments showed that 3º-hydrogens are even more reactive toward halogen atoms. Thus, light-induced chlorination of 2-methylpropane gave predominantly (65%) 2-chloro-2-methylpropane, the substitution product of the sole 3º-hydrogen, despite the presence of nine 1º-hydrogens in the molecule.

$(CH_3)_3CH$ + Cl_2 → 65% $(CH_3)_3CCl$ + 35% $(CH_3)_2CHCH_2Cl$

If you are uncertain about the terms primary (1º), secondary (2º) & tertiary (3º) Click Here.

It should be clear from a review of the two steps that make up the free radical chain reaction for halogenation that the first step (hydrogen abstraction) is the **product determining step**. Once a carbon radical is formed, subsequent bonding to a halogen atom (in the second step) can only occur at the radical site. Consequently, an understanding of the preference for substitution at 2º and 3º-carbon atoms must come from an analysis of this first step.

First Step: R_3CH + X· → R_3C· + H-X

Second Step: R_3C· + X_2 → R_3CX + X·

Since the H-X product is common to all possible reactions, differences in reactivity can only be attributed to differences in C-H bond dissociation energies. In our previous discussion of bond energy we assumed average values for all bonds of a given kind, but now we see that this is not strictly true. In the case of carbon-hydrogen bonds, there are significant differences, and the specific dissociation energies (energy required to break a bond homolytically) for various kinds of C-H bonds have been measured. These values are given in the following table.

R (in R–H)	methyl	ethyl	i-propyl	t-butyl	phenyl	benzyl	allyl	vinyl
Bond Dissociation Energy (kcal/mole)	103	98	95	93	110	85	88	112

The difference in C-H bond dissociation energy reported for primary (1º), secondary (2º) and tertiary (3º) sites agrees with the halogenation observations reported above, in that we would expect weaker bonds to be broken more easily than are strong bonds. By this reasoning we would expect benzylic and allylic sites to be exceptionally reactive in free radical halogenation, as experiments have shown. The methyl group of toluene, $C_6H_5CH_3$, is readily chlorinated or brominated in the presence of free radical initiators (usually peroxides), and ethylbenzene is similarly chlorinated at the benzylic location exclusively. The hydrogens bonded to the aromatic ring (referred to as phenyl hydrogens above) have relatively high bond dissociation energies and are not substituted.

$$C_6H_5CH_2CH_3 + Cl_2 \rightarrow C_6H_5CHClCH_3 + HCl$$

Contributors

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