

13.6: Chlorination versus Bromination

A Free Radical Substitution Reaction

This page gives you the facts and a simple, uncluttered mechanism for the free radical substitution reaction between methane and bromine. This reaction between methane and bromine happens in the presence of ultraviolet light - typically sunlight. This is a good example of a photochemical reaction - a reaction brought about by light.



The organic product is bromomethane. One of the hydrogen atoms in the methane has been replaced by a bromine atom, so this is a substitution reaction. However, the reaction doesn't stop there, and all the hydrogens in the methane can in turn be replaced by bromine atoms.

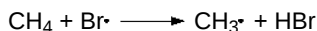
The mechanism

The mechanism involves a chain reaction. During a chain reaction, for every reactive species you start off with, a new one is generated at the end - and this keeps the process going. The over-all process is known as free radical substitution, or as a free radical chain reaction.

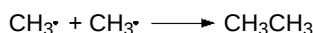
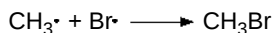
- **Chain initiation:** The chain is initiated (started) by UV light breaking a bromine molecule into free radicals.



- **Chain propagation reactions:** These are the reactions which keep the chain going.

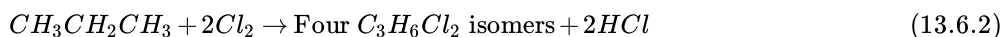


- **Chain termination reactions:** These are reactions which remove free radicals from the system without replacing them by new ones.

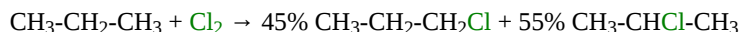


Selectivity

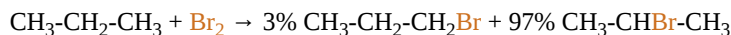
When alkanes larger than ethane are halogenated, isomeric products are formed. Thus chlorination of propane gives both 1-chloropropane and 2-chloropropane as mono-chlorinated products. Four constitutionally isomeric dichlorinated products are possible, and **five constitutional isomers** exist for the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



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 °C gives 45% 1-chloropropane and 55% 2-chloropropane.

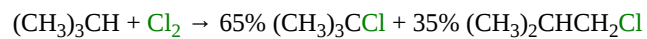


The results of bromination (light-induced at 25 °C) are even more suprising, with 2-bromopropane accounting for 97% of the mono-bromo product.



These results suggest strongly that 2°-hydrogens are inherently more reactive than 1°-hydrogens, by a factor of about 3:1. Further experiments showed that 3°-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 3°-hydrogen, despite the presence of nine 1°-hydrogens in the molecule.



Contributors

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