9.4: Chlorination vs Bromination

9.4.1 **Monochlorination**

First we will focus on monochlorination product, by assuming that chlorination only occur once. Since chlorine is a rather reactive reagent, it shows relative *low selectivity*, that means Cl_2 does not discriminate greatly among the different types of hydrogens atoms (primary, secondary or tertiary) in an alkane. As a result, for the reaction of alkane with different hydrogen atoms, a mixture of isomeric monochlorinated products are obtained.

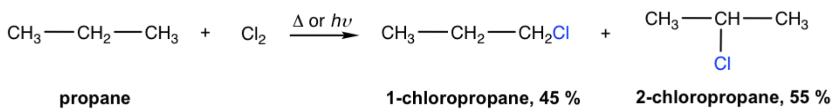


Figure 9.4a Monochlorination products

The experimental results of the monochlorination of propane indicate that 45% primary chloride (1-chloropropane) and 55% secondary chloride (2-chloropropane) are produced. How to explain this result?

To predict the relative amount of different chlorination product, we need to consider two factors at the same time: *reactivity* and *probability*.

It has been discussed in **section 9.3**, that different radicals (primary, secondary or tertiary) have different stability and reactivity. **The relative reaction rate of alkyl radicals for chlorination** have been measured and has the approximate values of:

tertiary 3°	: secondary 2°	: primary 1°
5.0	3.8	1.0

Figure 9.4b Relative reaction rate of alkyl radicals for chlorination

Probability simply depends how many hydrogen atoms are there for each type. With more hydrogen atoms available, the chance for that type of hydrogen to react is higher statistically.

So the overall amount of each isomeric product should be estimated by accounting for both reactivity and probability, that is:

the amount of a certain type of product = number of that type of hydrogens × relative reactivity

For the example of monochlorination of propane, the calculation is:

Amount of 1-chloropropane: 6 (number of 1°hydrogens) × 1.0 (relative reactivity) = 6.0

Amount of 2-chloropropane: 2 (number of 2°hydrogens) × 3.8 (relative reactivity) = 7.6

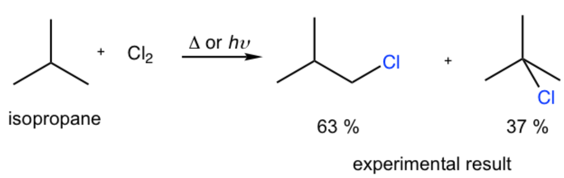
yield % of 1-chloropropane: 6.0/13.6 = 44 %

yield % of 1-chloropropane 7.6/13.6 = 56 %

The calculated values are consistent with the experiment results.

Exercises 9.1

Predict the percentage yield of each product for monochlorination of isobutane by calculation, and compare your calculated numbers to the experiment results. Are they consistent?



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For the alkane with only one type of hydrogen, the problem of isomeric mixture can be prevented of course since only one product produced. For the following chlorination of cylclopentane, only one monochloride is produced.

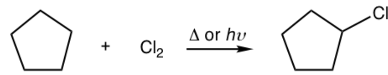


Figure 9.4c Chlorination of cylclopentane

9.4.2 **Multichlorination**

Although we assume that chlorination occurs once in last section discussions, this is not the actual case unfortunately. A common issue with chlorination is that multiple substitution always happen. A simple example is the chlorination of methane, that a mixture of multiple chlorination product were obtained as we learned before.

$$CH_4 + Cl_2 \xrightarrow{\Delta \text{ or } h\upsilon} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$$

(multi-chlorination products are possible for the reaction)

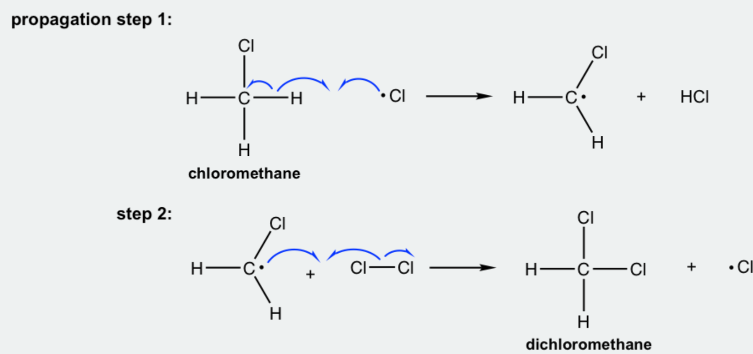
Figure 9.4d Example of multichlorination products

The mechanism for the formation of multichlorination product is similar to that of monochloride. When chloromethane (or methylchloride) reacts with Cl_2, another hydrogen is replaced by chlorine atom to give dichloromethane, dichloromethane reacts with Cl_2 again to give trichloromethane, and trichloromethane reacts further to produce tetrachloromethane. All the reactions still go through similar propagation steps with radical mechanism.

Examples

Show the mechanism of propagation steps for the formation of dichloromethane from chloromethane.

Solution:



Practically, to minimize the problem ofmultichlorination products, the reaction conditions can be controlled in certain ways, for example:

- Use high concentration of alkane relative to Cl_2, to decrease the possibility of multichlorination;
- Control reaction time: stop reaction after “short” time to favor monochlorination product.

These methods help to reduce the amount of multichlorination products, but the problem still cannot be completely avoided.

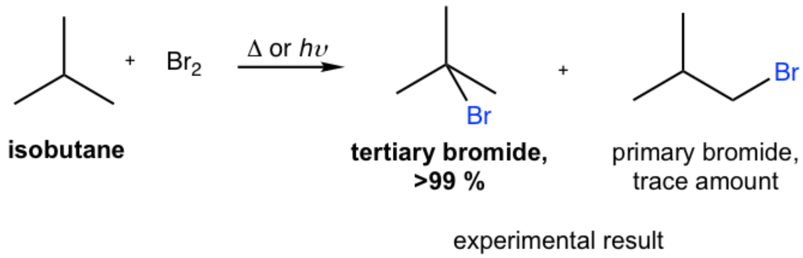
9.4.3 **Bromination**

Because of the two major problems for chlorination, lack of selectivity and multi-substitution, chlorination is not useful as a synthesis method to prepare a specific alkyl halide product. Instead, bromination with Br_2 can be applied for that purpose. The relative lower reactivity of bromine makes it exhibits a much greater selectivity. Bromine is less reactive, means it reactive more slowly, therefore it has chance to differentiate between the different types of hydrogens, and selectively reacts with the most reactive one. The relative reaction rate of bromination for different radical is shown here, and you can see the big difference to that of chlorination:

tertiary 3°	: secondary 2°	: primary 1°
1600	80	1.0

Figure 9.4e Relative reaction rate of bromination

For bromination, the reactivity difference between different types of position is so high that the reactivity factor become predominant for determining the product. Therefore **bromination usually occurs *selectively* on the most reactive position** (the position that forms the most stable carbon radical intermediate), and gives one major product exclusively, as the example here for bromination of isobutane.

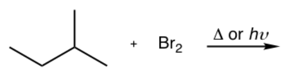


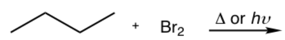
99%) + primary bromide, trace amount” width=”477″ height=”153″> Figure 9.4f An example of the bromination of isobutane

As a result, **bromination has the greatest utility synthesis of alkyl halide**.

Exercises 9.2

Show the major bromination product of following reactions.





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