THE REACTION BETWEEN SYMMETRICAL ALKENES AND BROMINE

Mechanism for the electrophilic addition reactions between bromine (and the other halogens)

The electrophilic addition of bromine to ethene

The facts

- Alkenes react in the cold with pure liquid bromine, or with a solution of bromine in an organic solvent like tetrachloromethane.
- The double bond breaks, and a bromine atom becomes attached to each carbon.
- The bromine loses its original red-brown colour to give a colourless liquid.
- In the case of the reaction with ethene, 1,2-dibromoethane is formed.

CH2=CH2 + Br2 → CH2-CH2 | | Br Br

- Decolourisation of bromine is often used as a test for a carboncarbon double bond.
- If an **aqueous solution of bromine** is used ("bromine water"), you'd get a mixture of products.
- The other halogens, apart from fluorine, behave similarly.
- (Fluorine reacts explosively with all hydrocarbons including alkenes to give carbon and hydrogen fluoride.)

The mechanism for the reaction between ethene and bromine

The reaction is an example of *electrophilic addition*.

Bromine as an electrophile

- The bromine is a very "polarisable" molecule and the approaching pi bond in the ethene induces a dipole in the bromine molecule.
- Write the words "induced dipole" next to the bromine molecule to show that you understand what's going on.

The simplified version of the mechanism



The more accurate version of the mechanism

In the first stage of the reaction, one of the bromine atoms becomes attached to both carbon atoms, with the positive charge being found on the bromine atom. A bromonium ion is formed.



The bromonium ion is then attacked from the back by a bromide ion formed in a nearby reaction.



THE REACTION BETWEEN UNSYMMETRICAL ALKENES AND BROMINE

An unsymmetrical alkene is one like propene in which the groups or atoms attached to either end of the carbon-carbon double bond are different.

For example, in propene there are a hydrogen and a methyl group at one end, but two hydrogen atoms at the other end of the double bond. But-1-ene is another unsymmetrical alkene.



The electrophilic addition of bromine to propene

The facts

- In common with all other alkenes, propene reacts in the cold with pure liquid bromine, or with a solution of bromine in an organic solvent like tetrachloromethane.
- The double bond breaks, and a bromine atom becomes attached to each carbon.
- The bromine loses its original red-brown colour to give a colourless liquid.
- In the case of the reaction with propene, 1,2-dibromopropane is formed.

CH₃CH=CH₂ + Br₂ → CH₃CH - CH₂ | | Br Br

The mechanism for the reaction between propene and bromine

The reaction is an example of *electrophilic addition*.

Bromine as an electrophile

- The bromine is a very "polarisable" molecule and the approaching pi bond in the propene induces a dipole in the bromine molecule.
- If you draw this mechanism in an exam, write the words "induced dipole" next to the bromine molecule.

The simplified version of the mechanism



The more accurate version of the mechanism

In the first stage of the reaction, one of the bromine atoms becomes attached to both carbon atoms, with the positive charge being found on the bromine atom. A bromonium ion is formed.



The bromonium ion is then attacked from the back by a bromide ion formed in a nearby reaction.



Halohydration of Alkenes



Reaction type: Electrophilic Addition

Summary

- Overall transformation : C=C to HO-C-C-X
- Electrophile : "X+"
- Reaction proceeds via cyclic halonium ion (compare with halogenation)
- The alternative nucleophile, water opens the halonium ion (instead of the halide ion)

- Regioselectivity : X reacts as the electrophile so the C-O bond forms at the more stable cation center.
- Stereoselectivity : **anti** since the two new s bonds form in separate steps.

MECHANISM FOR REACTION OF ALKENES WITH Br2 / H2O

Step 1:

Step 2:

Same first step as for the reaction of Br_2/CH_2CI_2 . The π electrons act as a nucleophile, attacking the bromine, displacing a bromide ion but forming a cationic cyclic bromonium ion as an intermediate.

Attack of the nucleophilic water molecule from the

side away from the bromonium center in an $S_N 2$ like fashion opens the cyclic bromonium ion to give

$: \overset{:}{B}_{r} \overset{:}{-} \overset{:}{B}_{r}^{+} : \overset{:}{B}_{r}^{-} : \overset{:}{B}_{r}^{-} : \overset{:}{B}_{r}^{-} : \overset{:}{B}_{r}^{-} : \overset{:}{B}_{r}^{-} : \overset{:}{B}_{r}^{+} : \overset{:}{B}_{r}^{-} : \overset{:}{H}^{+} : \overset{:}{B}_{r}^{+} : \overset{:}{B}_{r$

Step 3:

overall transaddition.

An acid / base reaction converts the oxonium into the alcohol.