Electrophilic substitution happens in many of the reactions of compounds containing benzene rings - the arenes. For simplicity, we'll only look for now at benzene itself. This is what you need to understand for the purposes of the electrophilic substitution mechanisms:

- Benzene, C₆H₆, is a planar molecule containing a ring of six carbon atoms each with a hydrogen atom attached.
- There are delocalized electrons above and below the plane of the ring.
- The presence of the delocalized electrons makes benzene particularly stable.
- Benzene resists addition reactions because that would involve breaking the delocalization and losing that stability.
- Benzene is represented by this symbol, where the circle represents the delocalized electrons, and each corner of the hexagon has a carbon atom with a hydrogen attached.

**Electrophilic substitution reactions involving positive ions**

**Benzene and electrophiles**

Because of the delocalized electrons exposed above and below the plane of the rest of the molecule, benzene is obviously going to be highly attractive to electrophiles - species which seek after electron rich areas in other molecules. The electrophile will either be a positive ion, or the slightly positive end of a polar molecule. The delocalized electrons above and below the plane of the benzene molecule are open to attack in the same way as those above and below the plane of an ethene molecule. However, the end result will be different.

If benzene underwent addition reactions in the same way as ethene, it would need to use some of the delocalized electrons to form bonds with the new atoms or groups. This would break the delocalization - and this costs energy. Instead, it can maintain the delocalization if it replaces a hydrogen atom by something else - a substitution reaction. The hydrogen atoms aren't involved in any way with the delocalized electrons. In most of benzene's reactions, the electrophile is a positive ion, and these reactions all follow a general pattern.
The general mechanism

The first stage

Suppose the electrophile is a positive ion \( \text{X}^+ \). Two of the electrons in the delocalized system are attracted towards the \( \text{X}^+ \) and form a bond with it. This has the effect of breaking the delocalization, although not completely.

\[ \text{H} \quad \text{X}^+ \rightarrow \text{H} \quad \text{X} \]

The ion formed in this step isn't the final product. It immediately goes on to react with something else. It is just an intermediate.

\[ \text{H} \quad \text{X} \rightarrow \text{H} \quad \text{X}^+ \]

There is still delocalization in the intermediate formed, but it only covers part of the ion. When you write one of these mechanisms, draw the partial delocalization to take in all the carbon atoms apart from the one that the \( \text{X} \) has become attached to. The intermediate ion carries a positive charge because you are joining together a neutral molecule and a positive ion. This positive charge is spread over the delocalized part of the ring. Simply draw the "+" in the middle of the ring. The hydrogen at the top isn't new - it's the hydrogen that was already attached to that carbon. We need to show that it is there for the next stage.

The second stage

\[ \text{Y}^+ \rightarrow \text{H} \quad \text{X} \rightarrow \text{Y} \quad \text{H} \]

Here we've introduced a new ion, \( \text{Y}^- \). Where did this come from? You have to remember that it is impossible to get a positive ion on its own in a chemical system - so \( \text{Y}^- \) is simply the negative ion that was originally associated with \( \text{X}^+ \). Don't worry about this at the moment - it's much easier to see when you've got a real example in front of you.
A lone pair of electrons on Y⁻ forms a bond with the hydrogen atom at the top of the ring. That means that the pair of electrons joining the hydrogen onto the ring aren't needed any more. These then move down to plug the gap in the delocalized electrons, so restoring the delocalized ring of electrons which originally gave the benzene its special stability.

The energetics of the reaction

The complete delocalization is temporarily broken as \(X\) replaces \(H\) on the ring, and this costs energy. However, that energy is recovered when the delocalization is re-established. This initial input of energy is simply the activation energy for the reaction. In this case, it is going to be high (something around 150 kJ mol\(^{-1}\)), and this means that benzene's reactions tend to be slow.

Electrophilic substitution reactions not involving positive ions

Halogenation and sulfonation

In these reactions, the electrophiles are polar molecules rather than fully positive ions. Because these mechanisms are different from what's gone before (and from each other), there isn't any point in dealing with them in a general way.

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