Objective

After completing this section, you should be able to use curved (curly) arrows, in conjunction with a chemical equation, to show the movement of electron pairs in a simple polar reaction, such as electrophilic addition.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- electrophilic
- nucleophilic

Pushing Electrons and Curly Arrows

Understanding the location of electrons and being able to draw the curly arrows that depict the mechanisms by which the reactions occur is one of the most critical tools for learning organic chemistry since they allow you to understand what controls reactions, and how reactions proceed.

Before you can do this you need to understand that a bond is due to a pair of electrons between atoms.

When asked to draw a MECHANISM, curly arrows should be used to show ALL the BONDING changes that occur.

A few simple lessons
Lesson 1

If we move the pair of electrons in a bond, then we BREAK that bond. This is true for single and multiple bonds as shown below:

\[ \text{H}_2\text{C}=\text{O}^- \rightarrow \text{H}_2\text{C}=\text{O}^+ + \text{H}^- \]  \hspace{1cm} \text{A reaction}

\[ \text{H}_2\text{C}=\text{O}^- \rightarrow \text{H}_2\text{C}=\text{O}^- + \text{H}^- \]  \hspace{1cm} \text{Resonance}

\[ \text{HCO}^+ \rightarrow \text{HCO}^- \]  \hspace{1cm} \text{Resonance}

Notice that since the starting materials were NEUTRAL, the products were also NEUTRAL.

In general terms, the SUM of the CHARGES on the starting materials MUST equal the SUM of the CHARGES on the products since we have the SAME NUMBER OF ELECTRONS.

The first example is a REACTION since we broke a sigma bond. In the second two examples, we moved pi electrons into lone pairs. This is RESONANCE.

If we move electrons between two atoms then we MAKE a new bond:

\[ \text{H}_2\text{C}=\text{O}^- \rightarrow \text{H}_2\text{C}=\text{O}^- + \text{H}^- \]  \hspace{1cm} \text{A reaction}

\[ \text{H}_2\text{C}=\text{O}^- \rightarrow \text{H}_2\text{C}=\text{O}^- + \text{H}^- \]  \hspace{1cm} \text{Resonance}

\[ \text{HCO}^+ \rightarrow \text{HCO}^- \]  \hspace{1cm} \text{Resonance}

We ALWAYS show the electrons moving from ELECTRON RICH to ELECTRON POOR.

Lesson 2
This is a simple acid/base reaction, showing the formation of the hydronium ion produced when hydrogen chloride is dissolved in water. It is useful to analyze the bond changes that are occurring. Water is functioning as a BASE and hydrogen chloride as an ACID.

Consider the reaction in discrete steps. Formation of a PROTON by the ACID which requires breaking the H-Cl bond which we do by taking the electrons OUT of the bond:

\[ \text{H}^+ + \text{Cl}^- \rightarrow \text{H}^+ \text{Cl}^- \]

Next, reaction of the BASE with the PROTON to make a new O-H bond. This requires that we put electrons BETWEEN the atoms that are to be BONDED:

\[ \text{H}^+ \text{O}^- \text{H} \rightarrow \text{H}_2\text{O}^- \]

However, we should consider this reaction as a single process, the BASE abstracting the PROTON from the ACID:

\[ \text{H}^+ \text{O}^- \text{H} \rightarrow \text{H}_2\text{O}^- \]

Notice that in each of these diagrams, the overall CHARGE of the reactants EQUALS that of the products.

We can also draw the curly arrows for the reverse reaction:

\[ \text{H}_2\text{O}^- \rightarrow \text{H}^+ \text{O}^- \text{H} \]

This shows the formation of the new H-O bond by taking electrons from the electron rich chloride ion and using them to make a bond to the H, and breaking the H-Cl bond by taking electrons out of the bond and giving them to the electron poor oxygen atom. Notice that the CHARGES BALANCE.
In this section we will look at the curly arrows for some NUCLEOPHILIC SUBSTITUTION reactions.

Overall the processes involved are similar to those for the ACID / BASE reactions we described above.

Overall in a nucleophilic substitution, a nucleophile (Nu) becomes bonded to C and a leaving group (LG) is displaced. In bonding terms this means we must MAKE a Nu to C bond and BREAK a C to LG bond.

Let's consider the stepwise SN2 reaction, for example the reaction of tBuCl with HO-. First we must remove the electrons from the C-Cl bond to break it:

Since we take electrons AWAY from C it becomes +ve carbocation and since we give them to Cl it becomes -ve chloride. In the second step the electron rich Nu donates electrons to form a new C-O bond with the C+.

In an SN2 process, the bond making and breaking occur simultaneously. Below we see the Nu donating electrons to form a new C-O bond and the C-Cl bond breaking by removing the electrons and giving them to the Cl. By making the bond changes simultaneously we avoid violating the octet rule at C.

Notice that in ALL steps the CHARGES of the starting materials BALANCE those of the products.

Lesson 4
In this section we will be looking at another substitution reaction but a little more involved. Let's consider the 
$\text{Sn}_2$ reaction of isopropyl bromide with water:

$$
\begin{array}{c}
\text{H}_3\text{C} - \text{C} - \text{Br} \\
\text{H}_3\text{C} - \text{OH} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
$$

First we should draw in the lone pairs. Once we have done that we should work out which bonds have been made and which have been broken.

$$
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\quad \text{MADE} \quad \text{C-O, H-Br}
\quad \text{BROKEN} \quad \text{C-Br, H-O}
$$

The curly arrows we draw must account for ALL of these bonding changes. Since we are dealing with an $\text{Sn}_2$ process the Nu must attack on the C undisplaced

$$
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\quad \text{H} + \text{O}^-
$$

Notice that these 2 arrows only show forming the C-O bond and breaking a Br bond and that overall the CHARGES BALANCE. Note that since the neutral C in water gave away electrons to form the new C-O bond it becomes positive in the intermediate formed. To complete the reaction we need to show making the H-Br bond and breaking an O-H bond. Notice that the CHARGES BALANCE!

$$
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\quad \text{H} + \text{O}^-
\quad \text{H} - \text{Br}^-
$$

Now for the mechanism of the reverse reaction, i.e. the reaction of isopropanol with hydrogen bromide to give isopropyl bromide:

$$
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\quad \text{MADE} \quad \text{O-H, C-Br}
\quad \text{BROKEN} \quad \text{C-O, H-BR}
$$

This mechanism must occur via the same pathway as the previous example (Law of Minimale Reversibility).

However, we should be able to deduce what happens without knowing that! First we know that HBr is a strong acid and therefore we should expect it to be a base. The most basic sites in the whole system are the lone pairs on the O. Since the lone pairs are electron rich, the arrows start there towards the proton:

$$
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\quad \text{H} - \text{Br}^- \\
\quad \text{H} + \text{O}^-
$$

The final part of the sequence is to make the bromide attack, donating electrons to form the new C-Br bond and here the leaving group, H$_2$O, break away taking the electrons from the C-O bond to neutralize the positive charge on the O.

Notice how the electrons flow from electron rich (negative) to electron poor (positive).

$$
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\rightarrow
\begin{array}{c}
\text{H}_3\text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{H} \\
\text{H}_3\text{C} - \text{Br}
\end{array}
\quad \text{H} - \text{Br}^- \\
\quad \text{H} + \text{O}^-
$$

**QUESTION:** Do the charges still balance in each step?

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**Curly Arrow Summary**

- Curly arrows flow from electron rich to electron poor.
- Therefore they start from lone pairs or bonds.
- The charges in any particular step should always be balanced.
- Remember to obey the rules of valence (e.g. octet rule for C, N, O, F etc.)
• If electrons are taken out of a bond, then that bond is broken.
• If electrons are placed between two atoms then it implies a bond is being made.

Exercises

Questions

Q6.6.1

Draw curved arrows to indicate mechanisms for the following reactions:

A) \[ \text{Br—Br} + \text{H—N—H} \rightarrow \text{Br}^- + \text{H—N—H} \]
B) \[ \text{O—O} + \text{Br} \rightarrow \]
C) \[ \text{O—Cl} \rightarrow \text{O}^- + \text{Cl}^- \]

Solutions

S6.6.1

A) \[ \text{Br—Br} + \text{H—N—H} \rightarrow \text{Br}^- + \text{H—N—H} \]
B) \[ \text{O—O} + \text{Br} \rightarrow \]
C) \[ \text{O—Cl} \rightarrow \text{O}^- + \text{Cl}^- \]
Contributors

- Dr. Ian Hunt, Department of Chemistry, University of Calgary
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)