Exercise 4: Pushing electrons

“Pushing electrons” is an informal term in chemistry, used to describe the elucidation of a resonance structure or reaction mechanism. In other words, using the curved arrow notation (as shown in the text), one can literally show the movement of electrons during a process. This type of representation (hopefully) makes clear how old bonds are broken and new ones are formed.

Resonance structures
Consider the allyl cation \( \text{CH}_2=\text{CHCH}_3^+ \). The curved arrow notation can be used to show that the \( \pi \) electrons in the double bond are attracted to the electron-deficient carbon and form a \( \pi \) bond between that carbon and the adjacent one. Notice that the electrons do not form a lone pair on the electron-deficient carbon; it’s not two electrons deficient!

Consider the acetate anion. The curved arrow notation is used to show that a lone pair of electrons on the electron-surfeited oxygen is attracted to the relatively electron-poor carbon (due to the withdrawl of electron density due to the carbonyl oxygen) and forms a \( \pi \) bond between it and that carbon. But wait! Two electrons is too many for the carbon to handle; fortunately there is a highly electronegative oxygen atom to draw the \( \pi \) electrons away from the old carbonyl bond and add them as a lone pair in its own valence shell.

Key points about using curved arrows:

• Always push electrons and never push positive charges.

• Always push electrons away from centers of negative charge and towards centers of positive charge.
1. Explain what is wrong about the following two scenarios for explaining how the allyl cation resonates.

\[ \text{CH}_2 = \text{CH}^- - \text{CH}_2^+ \]

Using the curved arrow notation, show (a) how the electron pairs move in the structure and (b) the final form of the resonance structure, if any, for the following ions:

2.

3.

4.

5.
Reaction mechanisms

The breakage of a \( \text{\textit{\textit{\textendash}} \text{\textit{\textendash}}} \) bond involves the movement of the bonding pair of electrons onto the more electronegative atom involved in the bond, where they will end up as a lone pair. Similarly, the formation of a \( \text{\textit{\textit{\textendash}} \text{\textit{\textendash}}} \) bond involves the attraction of the lone pair from an electron-rich species to a cation and the subsequent formation of a bond between them using these electrons.

\[
\begin{align*}
\text{CH}_3\text{C}^-\text{Cl}^- & \quad \rightarrow \quad \text{CH}_3\text{C}^+\text{Cl}^- \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

Key points in addition to the previous key points:

- Total charge is conserved. The sum of the charges on one side of the equation always equals the sum of the charges on the other.
- Electrons are conserved. The number of valence electrons on each side of an equation is always equal.

A \( \text{\textit{\textit{\textendash}} \text{\textit{\textendash}}} \) bond can be broken and another made simultaneously. Consider the mechanism below that shows the movement of two pairs of electrons: one pair leaving a nucleophile (Nu) to form a \( \text{\textit{\textit{\textendash}} \text{\textit{\textendash}}} \) bond with a carbon atom, and the other pair breaking a \( \text{\textit{\textit{\textendash}} \text{\textit{\textendash}}} \) bond to become a lone pair on an electrophilic leaving group (L)

\[
\begin{align*}
\text{Nu} & \quad \text{C}^-\text{L} & \quad \rightarrow \quad \text{Nu}^\text{+} \quad \text{C}^-\text{L} \\
\text{Nu} & \quad \text{Nu}^\text{+}
\end{align*}
\]

For the following pairs of reactants, show (a) the movement of electron pairs using the curved arrow notation and (b) the product.

6.