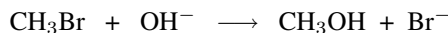


Curved Arrow Formalism

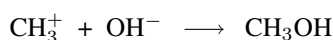
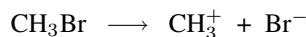
The sequence of steps by which a chemical reaction proceeds is called a **reaction mechanism**. The curved arrow formalism is a convenient method used by organic chemists to provide a better understanding for why each of these steps occurs in a particular order.

To illustrate this, consider the reaction:

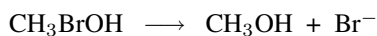
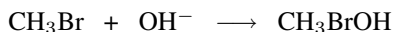


Looking at this reaction, three possible mechanisms seem reasonable.

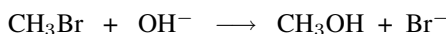
1. Loss of Br^- , followed by addition of OH^-



2. Addition of OH^- , followed by loss of Br^-



3. Loss of Br^- and addition of OH^- concurrently (both happening at the same time).



All three of these mechanisms lead to the right products, and as drawn above all seem 'reasonable'. By using the curved arrow formalism, it is possible to understand which one of this is most likely.

Rules

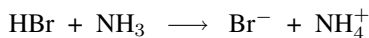
Curved arrows are designed to show the flow of electrons, not atoms. This appears 'backward', since we have typically focused on the movement of atoms. For example, the Bronsted-Lowry definition of an acid is an H^+ donor, and a base is an H^+ acceptor. The reason we focus on the movement of electrons is that this movement will almost always either create new bonds or break existing bonds, which is what is needed to understand how reactions occur. Electrons will generally flow *from* a region of high electron density (δ^-) such as a lone pair on an anion *to* a region of low electron density (δ^+).

To implement the curved arrow formalism, the following rules will be applied.

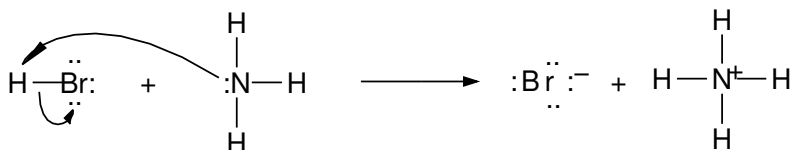
1. The tail of the arrow starts on the electrons present in the starting material.
2. The head of the arrow ends on the atom where the electrons will end up.

Using these rules, if a new bond is being formed, the arrow will connect the two atoms that will contain the new bond. If atoms are moving to become a lone pair, the arrowhead will point to the atom that ends up with the new lone pair of electrons.

To illustrate this procedure, consider the reaction:



In this reaction, HBr is the acid (proton donor), and NH_3 is the base (proton acceptor). The curved arrow mechanism for this reaction is shown below.



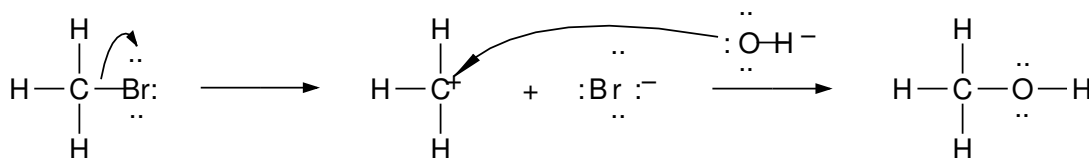
Several features are apparent from this example. First, it is essential that complete Lewis structures (including all lone pairs) be drawn before starting these types of problems. Second, more than one arrow can be drawn in any step. In this example, the formation of the N-H bond would give a hydrogen atom with too many bonds. To 'fix' this, the electrons in the H-Br bond move away to break the H-Br bond and become a lone pair on the Br^- at the same time the new N-H bond is forming.

The 'top' arrow in this mechanism flows from the lone pair of electrons on nitrogen (e^- rich region) to the H atom. Based on electronegativities, this bond is polarized $\delta^+ \text{H}-\text{Br}^{\delta-}$, so this flow of electrons is consistent with the principles presented above. The 'lower' arrow serves to remove electrons from the H-Br bond and moves them onto the more electronegative bromine atom. While the H-Br bond is not particularly 'electron-rich', addition of electrons from the formation of the N-H bond make this bond much more reactive.

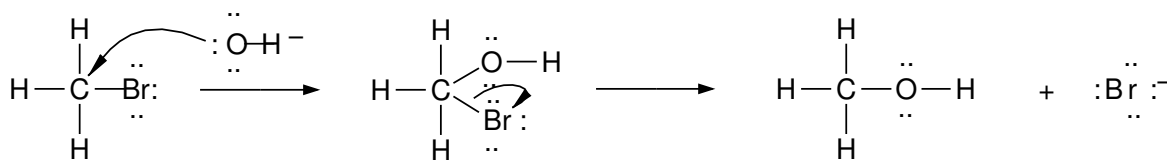
Finally, it is worthwhile to mention that the curved arrow formalism fits in very well with the **Lewis definition** for acids and bases. By this definition, the acid is the electron pair acceptor (in this example HBr) and the base is the electron pair donor (in this example NH_3). The acids and bases have not changed (HBr is still the acid), just the definitions (H^+ donor vs. e^- pair acceptor).

Understanding reactions

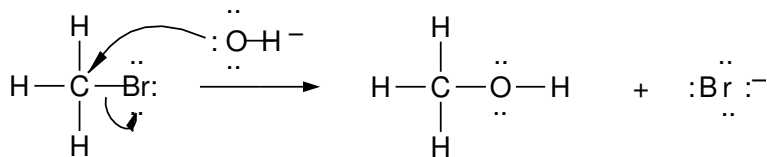
Let's look at the $\text{CH}_3\text{Br} + \text{OH}^-$ reaction again and show the curved arrow formalism for each of the three proposed mechanisms. For the first mechanism, loss of Br^- results in a carbon with only 3 bonds and a positive formal charge. While this type of **carbocation** can occur as the intermediate in a reaction mechanism, it is typically only observed if the carbocation is surrounded by bulky, electron-donating groups. Since this first mechanism requires formation of a carbocation that is *not* stabilized (the carbon is surrounded by 3 hydrogen atoms), the fact that this mechanism requires formation of such an unstable intermediate means that it is not an ideal choice for this reaction.



The second mechanism we proposed is shown below. For this reaction, the carbon atom in the intermediate contains five bonds. This is highly unstable and even less likely than the carbocation proposed for the first mechanism. Thus, we can eliminate this second mechanism from consideration.



The final mechanism involves the simultaneous formation of a C-O bond and breaking of a C-Br bond. This mechanism has the advantage of *not* forming any unstable intermediates. The most serious limitation is the fact that five atoms need to be *close* to the carbon while the reaction is occurring. This is not a problem *if* the carbon does not have bulky groups bonded to it. In this example, the three groups that do not change are all H atoms (which are as small as you can get), so this mechanism appears to be the most reasonable of the three and is the generally accepted mechanism for this reaction.

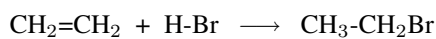


Based on the above analysis, we might predict that the reaction of 2-bromo-2-methylpropane with hydroxide (shown below) might proceed by the first mechanism proposed above because (1) the carbon atom is surrounded by three groups that might make it difficult to get five atoms close to the central carbon and (2) the carbocation intermediate is protected and stabilized by the presence of the three CH₃ groups.

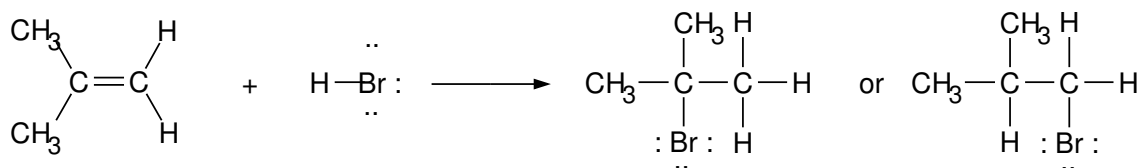


Addition to C=C bonds

When H-Br reacts with an alkene (a compound containing a C=C), the carbon-carbon double bond becomes a carbon-carbon single bond and new C-H and C-Br bonds are formed, one on each of the alkene carbon atoms. For example:

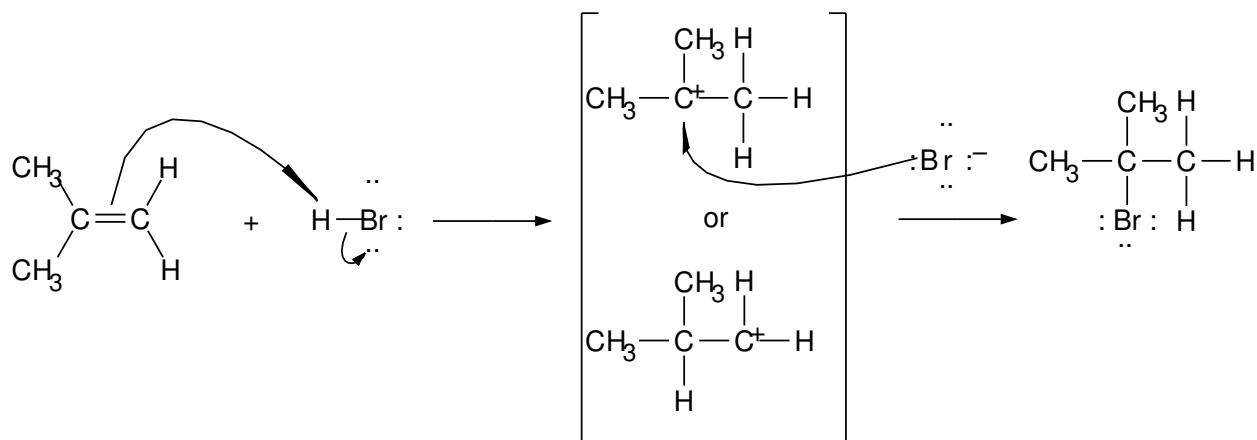


If different groups are attached to the two ends of the C=C, then two possible products can be formed. For example:



Both of these reactions follow the pattern for addition seen in the first example. However, if this reaction is performed in the lab, one of these products is formed in much higher yield than the other product. This can be explained by looking at the mechanism proposed for this reaction.

In the first step, the electrons in the C=C attack the hydrogen atom in H-Br, forming a carbocation (C⁺). In the top intermediate shown, this carbocation is protected and stabilized by three carbon groups. In the lower intermediate, the carbocation is only bound to one carbon group and two H atoms. Since this carbocation is expected to be much less stable, the major product comes from the addition of Br⁻ to the upper intermediate (the more stable carbocation).

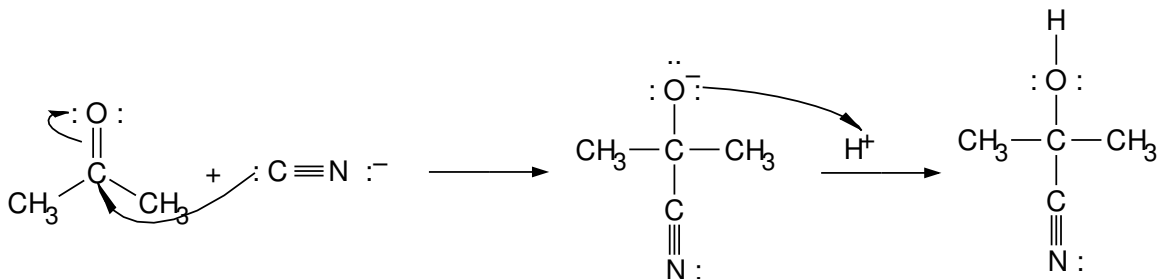


Reactions of Carbonyl Groups

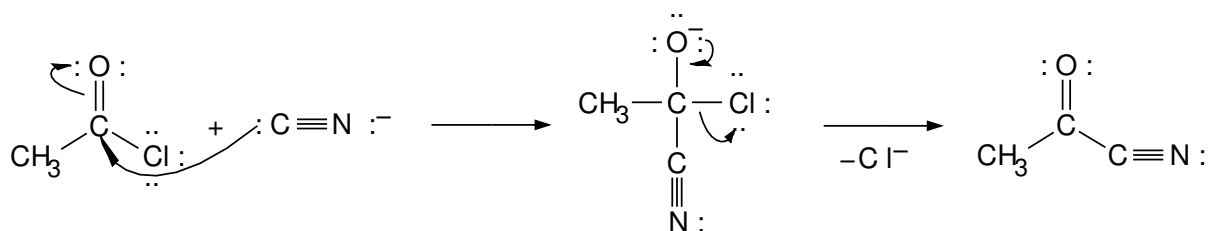
The C-O bond is a very polar bond. Due to the electronegativity of the groups involved, the C atom has a significant partial positive charge (δ^+) and the oxygen atom has a partial negative charge (δ^-). If a carbonyl group reacts with

a compound containing a strongly negative reactive center (such as $\text{:C}\equiv\text{N:}^-$), this compound will attack the carbon atom of the carbonyl.

What happens next depends on the starting material used. For some compounds, attack of the carbonyl gives rise to a negatively charged oxygen that 'picks up' a proton to become an O-H group. An example of this is shown for the reaction of acetone with CN^- . This type of reaction is referred to as an **addition reaction**.



However, in some cases the C=O bond is reformed and a group present in the original carbonyl is 'lost'. The reaction below shows this **substitution reaction**.



In both cases the first step is identical: the negatively charged CN^- group attacks the carbonyl carbon atom and the C=O becomes C-O⁻. The difference is in the second step. In the first example, the intermediate formed remains essentially intact and the only change is the addition of H⁺. In the second example, the C=O bond is reformed and the C-Cl bond is broken.

What causes this difference? One explanation is that the C-Cl bond is much weaker than the C-CH₃ bond, so it is easier to break the C-Cl bond and lose the Cl⁻ group. A closely related explanation is that the Cl⁻ is a relatively stable **leaving group**, so formation of this ion in solution is energetically favorable. If the C-CH₃ bond were to break, a CH₃⁻ group would be formed that is *not* stable (carbon wants to have four bonds, and is not electronegative enough to *want* to carry a negative charge). Both explanations focus on the stability of the leaving group. If a group is easy to lose (weak C-group bond) and the group is stable in solution, then the substitution pathway is favored. Otherwise, the addition pathway is preferred.

Summary

When seeing this for the first time, the curved arrow formalism does not appear to be an intuitive way of looking at reaction mechanisms. However, it is a very powerful technique that can often provide understanding of chemical reactions. With practice and a thorough understanding of chemical principles, the curved arrow formalism can be a useful tool for predicting the outcome of chemical reactions. For this class, our goal is to use the curved arrow formalism as a means of reducing the amount of pure memorization and replacing with an understanding of some of the reactions that we will cover this semester.