Making Sugars

The reactions that take carbon dioxide to sugar involve nucleophilic attack at the carbon of carbon dioxide and reduction. The reducing equivalents come from NADPH. Energy is transmitted to the intermediate molecules by transfer of a phosphate group from ATP.

A nucleophile is a molecule that is electron-rich, has an available electron pair, and can form a bond with another atom. When the nucleophile reacts with a proton to form a bond, it is a base. Lewis and Bronsted bases are sub-sets of nucleophiles.

Nucleophiles react with electrophiles. Electrophiles are electron-poor and capable of forming a new bond with another atom.

Outline

• Carbon Dioxide
• Reaction Steps
• Calvin Cycle
• Homework

At right is a field of sugar cane.

Carbon Dioxide

Properties of Carbon Dioxide

From the Lewis structure of CO$_2$ and VSEPR, we can determine that this is a linear molecule.

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]
Let's look at some of the physical properties of CO₂.

The C-O bonds in carbon dioxide are polar and yet the dipole moment is zero because the 2 bond dipoles cancel each other.

**Electronegativity:**

\[
\text{O} = 3.5 \\
\text{C} = 2.5
\]

**Bond polarity** = 3.5 - 2.5 = 1.0

**Dipole moment** = 1.0 - 1.0 = 0.0

<table>
<thead>
<tr>
<th>Property</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>boiling point</td>
<td>195 (sublimes)</td>
</tr>
<tr>
<td>( \Delta H_f ) (298 K)</td>
<td>-393.5 kJ/mol</td>
</tr>
<tr>
<td>bond energy</td>
<td>806 kJ/mol</td>
</tr>
<tr>
<td>C-O bond distance</td>
<td>1.16 Å</td>
</tr>
<tr>
<td>dipole moment</td>
<td>0 D</td>
</tr>
</tbody>
</table>

One thing that we can understand by looking at the structure of CO₂, is that the carbon center of the molecule must be **electrophilic**. An **electrophile** (electron-lover) is a center that is electron poor and will be attracted to centers that are electron-rich.

Even though the total electron count around the carbon is 8, this overestimates the electron density. This carbon is bonded only to highly electronegative oxygen atoms. The bonding electrons will all be more closely associated with oxygen than with carbon.

**Bonding in Carbon Dioxide**

From the Lewis structure we can see that the carbon in CO₂ must make 2 sigma bonds and it has no lone pairs. This atom will be 2sp hybridized with remaining 2px and 2py atomic orbitals.

Each oxygen makes 1 sigma bond and also needs 2 orbitals for lone pairs of electrons. These must each be 2sp² hybridized with a remaining 2p orbital. One of the oxygens will have a 2px orbital to combine with the carbon 2px orbital. The other oxygen will have a 2py orbital that can combine with the other p orbital on carbon.

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A 2sp² orbital on O₁ combines with a 2sp orbital on C to make a sigma bonding and a sigma antibonding molecular orbital. The other 2sp orbital on C combines with a 2sp² orbital on O₂ to make another set of sigma bonding and sigma antibonding molecular orbitals.

The remaining 2sp² from the oxygen atoms become non-bonding molecular orbitals.

The O¹ 2pₓ combines with the C 2pₓ to make a pi bonding and pi antibonding molecular orbital. The O² 2pᵧ combines with the C 2pᵧ to make another set of pi bonding and pi antibonding molecular orbitals.

The 16 valence electrons fill through the 2 pi bonding orbitals so there is a full double bond between carbon and each oxygen.

**Oxidation States**

As you saw above, the total electron count around the atoms in carbon dioxide seriously overestimates the electron density around the carbon atom. It doesn't help us predict the reactivity of this atom. The oxidation state formalism can give us a better idea about the electron density around an atom and its tendency to add electrons and become reduced.

To find the oxidation state of atoms in CO₂,

1. Draw the Lewis structure.
2. Break the bonds giving all of the bonding electrons to the more electronegative of the 2 atoms. (When the atoms are the same, give each atom 1/2 of the bonding electrons.)

3. Count the electrons around each atom and compare the number of electrons to the number of valence electrons, just as you do for formal charge.

4. Use Roman numerals instead of numbers to designate the oxidation state.

\[
\begin{array}{ccc}
\text{O} & \text{C} & \text{O} \\
\text{break} & \text{bonds} & \text{IV} & \text{C} & \text{IV} & \text{-II} \\
\text{O electrons here} & -8 & \text{C electrons here} & 0 & \text{C valence electrons} & -4 & \text{O oxidation state= 0 -(-4) = +4 or IV} \\
\text{O valence electrons} & -6 & \text{O oxidation state} & -8 -(-6) = -2 \text{ or -II} & \text{O oxidation state} & -8 -(-6) = -2 \text{ or -II}
\end{array}
\]

From the oxidation states, we see that the carbon center is very electron poor and in its highest possible oxidation state. It should be susceptible to reduction.

**Reductive Coupling**

Sodium metal has a single electron in its valence shell. It has a strong tendency to lose that electron and become oxidized. Carbon in CO\(_2\) is in its highest oxidation state. It should have a tendency to gain an electron and become oxidized.

\[
\begin{array}{cccc}
Na^+ & \text{IV} & \text{-II} & \text{O} \\
\text{Na}^+ & + & \text{O} = \text{C} = \text{O} & \text{Na}^+ \\
\text{O}^2- & \text{O} = \text{C} = \text{O} & \text{Na}^+ & \text{Na}^+ \\
\end{array}
\]

The unpaired electrons on two of the reduced carbon centers can combine to form a covalent bond in the product, sodium oxalate.

\[
\begin{array}{cccc}
\text{Na}^+ & \text{O}^2- & \text{O} = \text{C} = \text{O} & \text{Na}^+ \\
\text{Na}^+ & \text{O}^2- & \text{O} = \text{C} = \text{O} & \text{Na}^+ \\
\end{array}
\]

**Hydroxide Addition**

The carbon of CO\(_2\) is electrophilic (electron-poor). The oxygen in hydroxide ion, HO\(^-\), has excess electron density on oxygen. An electron-rich center that can form a bond with an electron-poor carbon atom is called a nucleophile (positive charge-lover). The purple arrows in the reaction scheme indicate the flow of electrons in the reaction.
Carbon Dioxide to Sugar

Enzyme-sugar Complex as a Nucleophile

One step in the production of sugar from carbon dioxide involves a carbon nucleophile adding to the electrophilic carbon of carbon monoxide.

The carbon nucleophile is created by the reaction of an enzyme called RuBisCo binding and activating a 5-carbon sugar molecule (ribulose 1,5-bisphosphate).

Enzymes are large proteins that can catalyze reactions by binding and modifying the substrates so that the reactants can combine through a pathway that has a lower activation barrier. The RuBisCo enzyme is shown at right.

We can think about the enzyme (like a base) removing a proton from ribulose 1,5-bisphosphate to put a negative charge on one of the carbon atoms. That carbon atom would be nucleophilic, just like the oxygen in hydroxide ion. It would react in the same way, using its pair of electrons to form a bond to the carbon of CO₂. The proton taken by the enzyme could then be transferred to the negatively charged oxygen of the product molecule.
As soon as the product is released into the water solution around the enzyme, it reacts with water to give two, 3-carbon pieces.

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**Adding Energy with ATP**

An ATP molecule, produced in the light reaction of photosynthesis, reacts with each of the 3-carbon pieces. ATP transfers a phosphate group and energy to the product. Phosphate groups in water can lose 1 or 2 other their acidic protons, depending on the pH of the solution. The fully protonated molecules are shown below.
Reduction by NADPH
Remember that another product of the light reaction was NADPH. This results from the transfer of 2 electrons and a proton to NADP⁺.

NADPH can deliver those 2 electrons and 1 proton (or H⁺) to the carbon derived from carbon dioxide. The product is a 3-carbon sugar, glyceraldehyde 3-phosphate.

Calvin Cycle
On the last page you saw the reactions that convert carbon dioxide and ribulose 1,5-bisphosphate into 2 equivalents of glyceraldehyde 3-phosphate. These are part of the Calvin cycle.
If this series of reactions occurs 6 times (6 equivalents of CO₂), 12 equivalents of glyceraldehyde 3-phosphate would be produced.

- 10 react in a series of steps to re-form 6 ribulose 1,5-bisphosphates

- 2 form a 6-carbon sugar, glucose.
Ultimately, all of the carbons of ribulose come from CO$_2$. A balanced reaction for the formation of the glyceraldehyde-3-phosphate is:

$$3 \text{CO}_2 + 6 \text{NADPH} + 5 \text{H}_2\text{O} + 9 \text{ATP} \rightarrow \text{C}_3\text{H}_5\text{H}_3\text{O}_3\text{P}_2\text{H}_2 + 2 \text{H}^+ + 6 \text{NADP}^+ + 9 \text{ADP} + 8 \text{H}_2\text{PO}_4^-$$