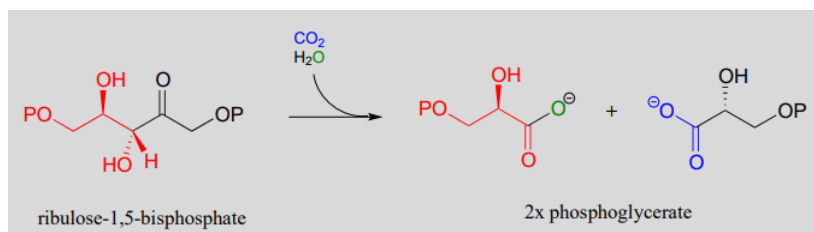


## 13.6: Carboxylation

It is difficult to overstate the importance to biology and ecology of the enzymatic reaction we are going to see next: ribulose 1,5-bisphosphate carboxylase (Rubisco) plays a key role in closing the 'carbon cycle' in our biosphere, catalyzing the incorporation of a carbon atom - in the form of carbon dioxide from the atmosphere - into organic metabolites and eventually into carbohydrates, lipids, nucleic acids, and all of the other organic molecules in living things. Rubisco is probably the most abundant enzyme on the planet.

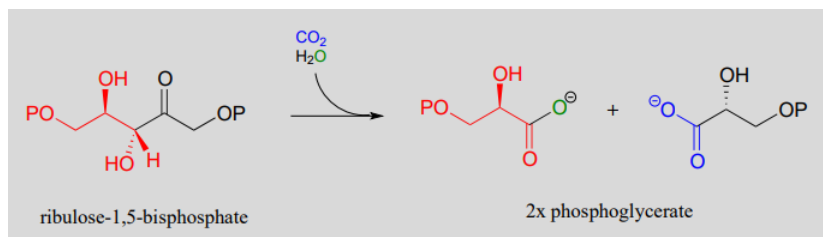
You can think of a carboxylation reaction as essentially a special kind of aldol reaction, except that the carbonyl electrophile being attacked by the enolate is  $CO_2$  rather than a ketone or aldehyde:

Mechanism for carboxylation of an enolate

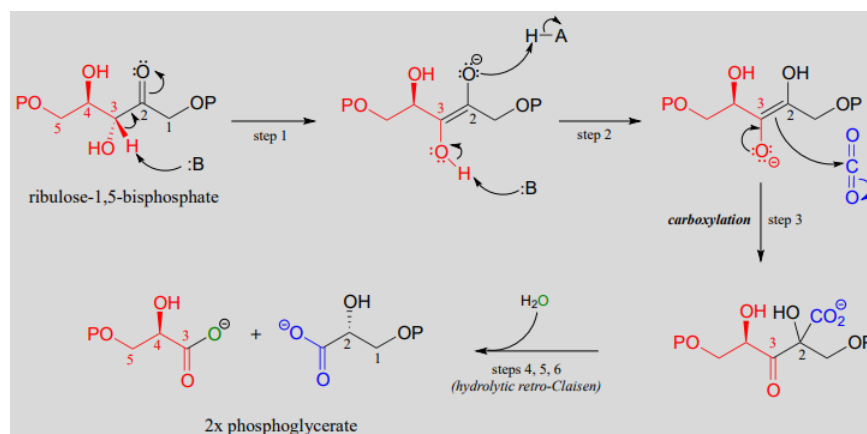


Here is the full Rubisco reaction. Notice that the carbon dioxide (in blue) becomes incorporated into one of the two phosphoglycerate products.

The Rubisco reaction:



Mechanism:



The mechanism for the Rubisco reaction is somewhat involved, but if we break it down into its individual steps, it is not terribly difficult to follow. In step 1, an  $\alpha$ -carbon on ribulose 1,5-bisphosphate is deprotonated to form an enolate. In step 2, the oxygen at carbon #3 is deprotonated while the oxygen at carbon #2 is protonated: combined, these two steps have the effect of creating a different enolate intermediate and making carbon #2, rather than carbon #3, into the nucleophile for an aldol-like addition to  $CO_2$  (step 3). Carbon dioxide has now been 'fixed' into organic form - it has become a carboxylate group on a six-carbon sugar derivative. Steps 4, 5, and 6 make up a hydrolytic retro-Claisen cleavage reaction (in other words, water is the bond-breaking

nucleophile) producing two molecules of 3-phosphoglycerate. Phosphoglycerate is channeled into the gluconeogenesis pathway to eventually become glucose.

### ? Exercise 13.6.1

Draw out the full mechanism for steps 4-6 in the Rubisco reaction.

This page titled [13.6: Carboxylation](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [Tim Soderberg](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.