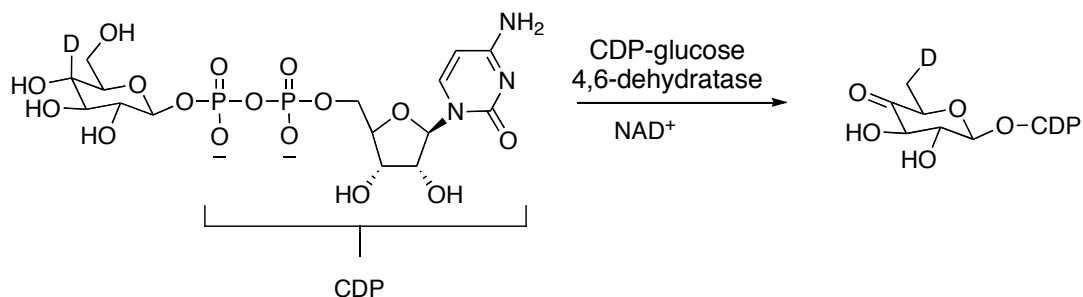
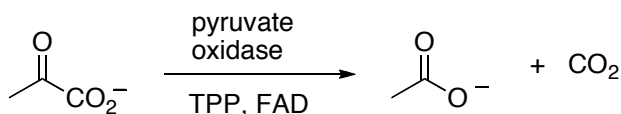


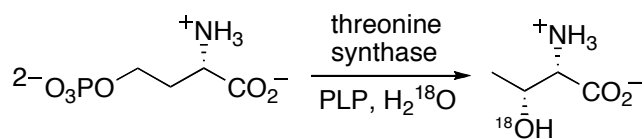
The enzyme CDP-glucose-4,6-dehydratase catalyzes the conversion below and requires a catalytic amount of NAD^+ for activity. Suggest a mechanism that is consistent with the transfer of the deuterium (D) label.



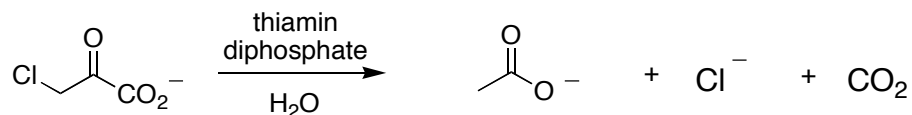
Pyruvate oxidase catalyzes the oxidative decarboxylation of pyruvate to acetate. The enzyme requires thiamine diphosphate (TPP) and FAD as cofactors and utilizes O_2 as the ultimate electron acceptor. Suggest a mechanism for the reaction.



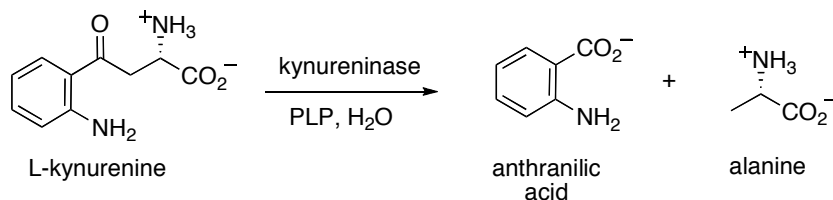
Threonine synthase is a pyridoxal phosphate (PLP) dependent enzyme that catalyzes the conversion of L-homoserine phosphate to L-threonine. An ^{18}O label is incorporated at the sidechain hydroxyl group of threonine when the reaction is carried out in ^{18}O -labeled water. Suggest a mechanism for the reaction that is consistent with this observation.



Halogenated hydrocarbons are potentially toxic industrial contaminants. They can be metabolized to 3-halopyruvic acid and further enter various cellular pathways. An enzyme that utilizes thiamine diphosphate as a cofactor from a microorganism has been found to convert 3-chloropyruvic acid to acetate, chloride ion, and CO_2 . Give a complete mechanism for the reaction.



Kynureninase is a pyridoxal phosphate-dependent enzyme that catalyzes the conversion of L-kynurenine to anthranilic acid and alanine. If the reaction is run in deuterated water (D_2O), a deuterium label is incorporated at the α -position of alanine. Suggest a mechanism for the reaction.



Benzylformate decarboxylase is a thiamine diphosphate-dependent enzyme that catalyzes the decarboxylation of benzylformate (PhCOCO_2H) to benzaldehyde (PhCHO) and CO_2 . The phosphonic acid shown below is an analogue of benzylformate and inhibits the enzyme. The overall inhibition reaction involves the formation of benzaldehyde and phosphorylation of an active site serine. Give a detailed mechanism for the inhibition reaction.

