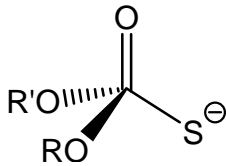


Chapter 10 Solutions

1) Comparing the water exchange rate of $[\text{Fe}(\text{OH}_2)_6]^{3+}$ with $[\text{Zn}(\text{OH}_2)_6]^{2+}$, we note that the zinc complex is five orders of magnitude more labile. Presumably, trivalent iron or manganese will bind substrates too strongly to have effective catalytic hydrolysis (too slow a turnover rate).

2) See slides 34 and 35 of lecture 8.

3) Substituting an oxygen atom with a sulfur will produce a chiral center at the phosphorus in a nucleotide backbone. Depending on the mechanism of the enzyme that processes the phosphate ester, there will be inversion or retention of stereochemistry at the phosphorus.



4) For example, in alkaline phosphatase, two protons on Arg₁₆₆ hydrogen bond to two of the phosphate oxygens. Presumably, this partially negates the negative charges on the oxygens, thus promoting nucleophilic attack on the phosphorus. An experimenter could mutate this to an alanine or glutamate, which would presumably decrease or inhibit reactivity.

5) Presumably, the zinc in carboxypeptidase withdraws electron density from the carbonyl carbon through the carbonyl oxygen to which it is bound. In a similar manner, NH groups could effect a withdrawal of electron density by hydrogen bonding to the carbonyl oxygen. Decreasing the electron density at the carbonyl carbon promotes nucleophilic attack.