Basis for High Free Energy of Hydrolysis

Phosphate ester hydrolysis releases much less free energy than ATP phosphoanhydride hydrolysis. Why? A typical phosphate ester hydrolysis would proceed as follows:

$$\text{Glycerol-1-phosphate} + H_2O \rightleftharpoons \text{Glycerol} + P_i \quad \Delta G'^{\circ} = -9.2\ \text{kJ/mol} \qquad (8\text{-}4)$$

The difference is due to the resonance stabilization of ADP and P_i (products of hydrolysis) versus ATP, and the greater electrostatic repulsion of charges in ATP versus products ADP and P_i. These factors do not apply to hydrolysis of standard phosphoesters.

Other biochemicals also have a high free energy of hydrolysis or of phosphoryl group transfer—namely, phosphocreatine phosphate (important in muscles) and phosphoenolpyruvate. Their reaction can also help drive coupled reactions toward the formation of (otherwise unlikely amounts of) product.

In ATP and these other compounds, the phosphoanhydride bonds are normal chemical bonds, not bonds where the electrons are excited. They simply have a large free energy release when hydrolyzed. Don't be misled by terminology like "high-energy bonds."

Coenzyme A: Carrier of Activated Acyl Groups

The name coenzyme A is often abbreviated to CoA; the "A" comes from the adenosine nucleotide part of the structure. To emphasize the role of the reactive thiol group, we shall occasionally use the abbreviation CoASH instead of CoA.

Structure of Coenzyme A

Figure 8-14 shows the detailed structure of *coenzyme A*. There are three major parts here: the adenine nucleotide, the *pantothenic acid* moiety (vitamin B_5), and the *mercaptoethylamine*. This last group carries the main reactive site, a thiol group. Note the use of the nucleotide "handle" for holding the coenzyme on the enzyme. Many enzymes have a special pattern of folding of the polypeptide chain to form a site on the protein surface that will specifically hold or bind the adenosine moiety.

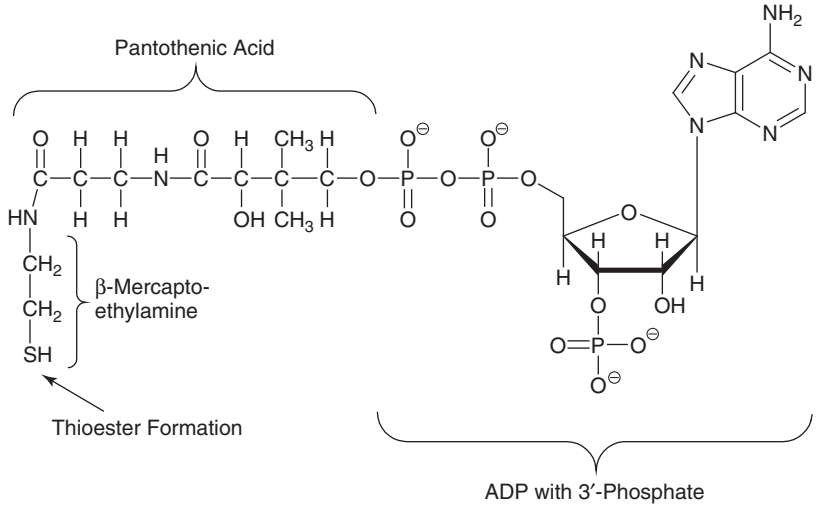

Figure 8-14 Structure of coenzyme A.

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