Coenzyme or Prosthetic Group	Subunit (Attachment/*Name*)	Function of Subunit/ Coenzyme/Group
TPP	E_1 (tight but noncovalent) (*pyruvate decarboxylase*)	Nucleophilic attack on pyruvate, expulsion of CO_2, formation of hydroxyethyl group
Lipoic acid	E_2 (attached to Lys) (*dihydrolipoyl transacetylase*)	Accept acetyl group from TPP, pass it on to CoA and regenerate TPP (act as intermediate electron carrier)
Coenzyme A	Free in solution (binds to E_2)	Accept acetyl group from lipoamide, generate reduced lipoamide (act as intermediate electron carrier)
FAD	E_3 (tight but noncovalent) (*dihydrolipoyl dehydrogenase*)	Accept electrons from reduced lipoamide, transfer them to NAD^+
NAD^+	Free in solution (binds to E_3)	Accept electrons from $FADH_2$ and regenerate FAD

Table 10-1 Cofactors and Subunits of the Pyruvate Dehydrogenase Complex

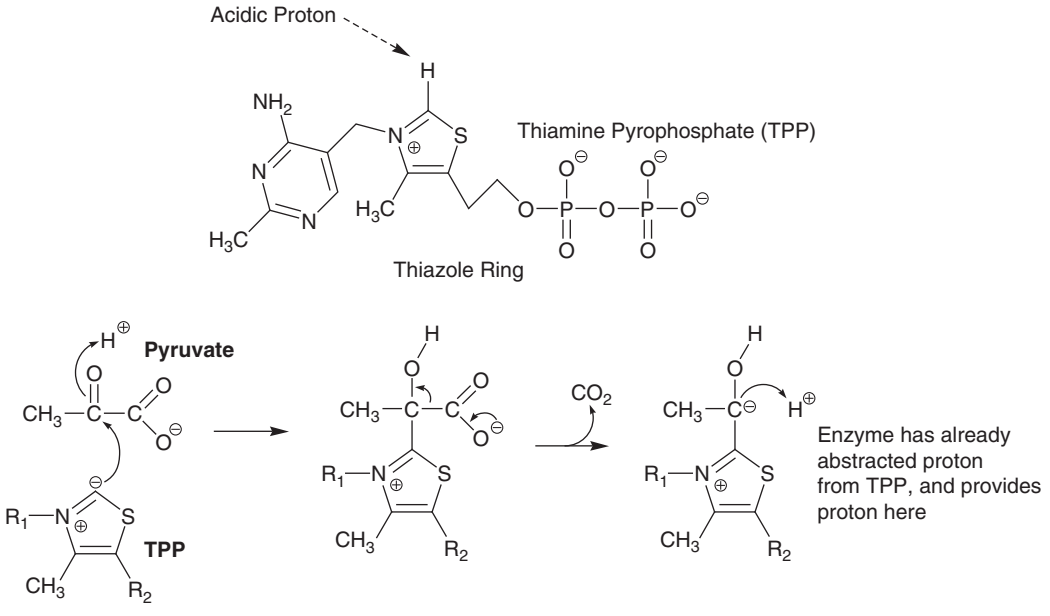

Figure 10-6 Structure of thiamine pyrophosphate (TPP), showing the acidic carbon of the thiazole ring, with details of the thiazole carbanion attack on pyruvate.

dehydrogenase, and transketolase). It helps in many different reactions. Broadly speaking, it plays two major roles, in the following processes:

- Degradation of α-keto acids, as with the enzymes pyruvate dehydrogenase and α-ketoglutarate dehydrogenase, via either non-oxidative decarboxylation or oxidative decarboxylation
- Transketolization (in connection with reactions of carbohydrates; see Chapter 12)

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