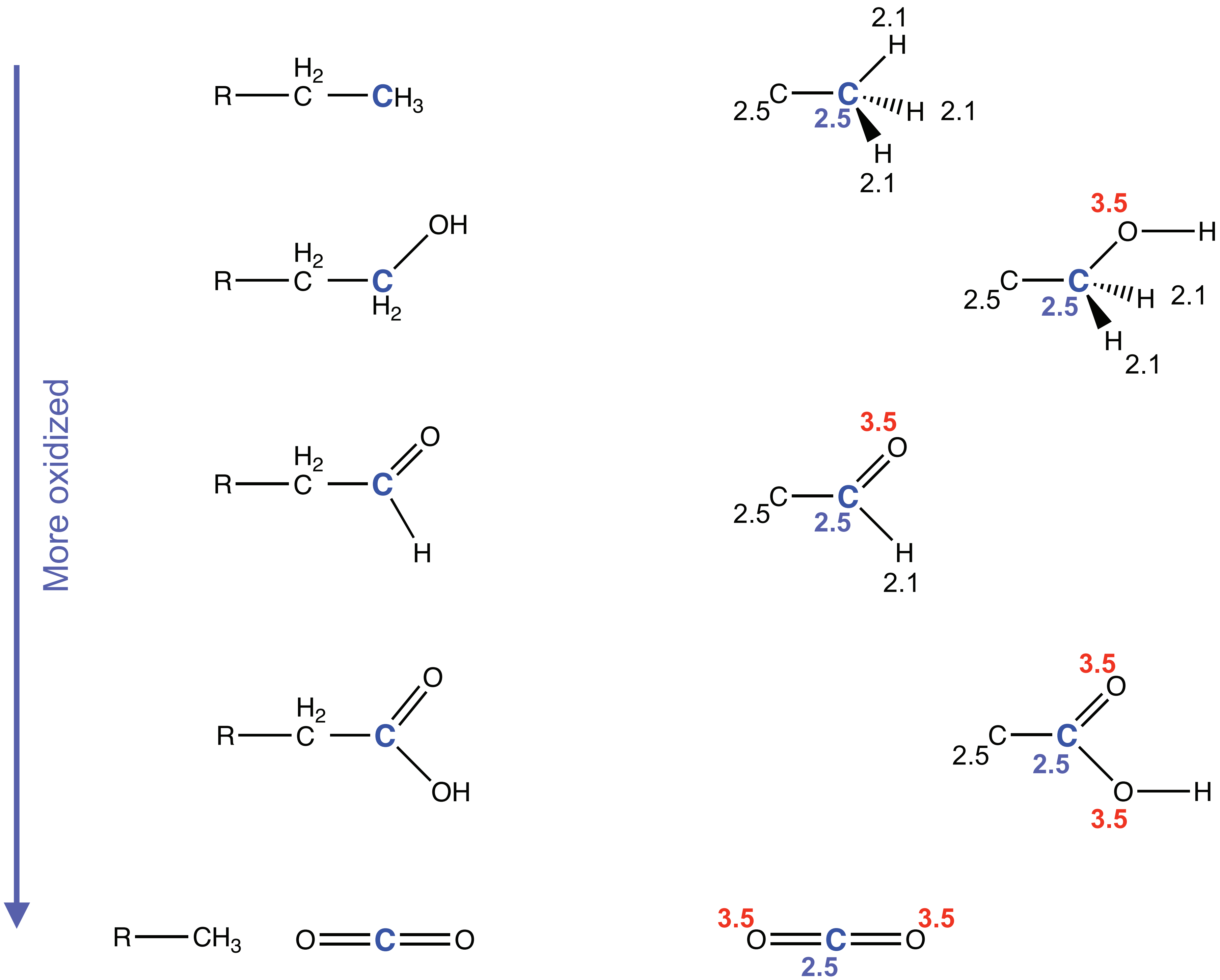
Complete combustion of which produces more energy?

1) Ethanol

2) Ethane


More oxidized

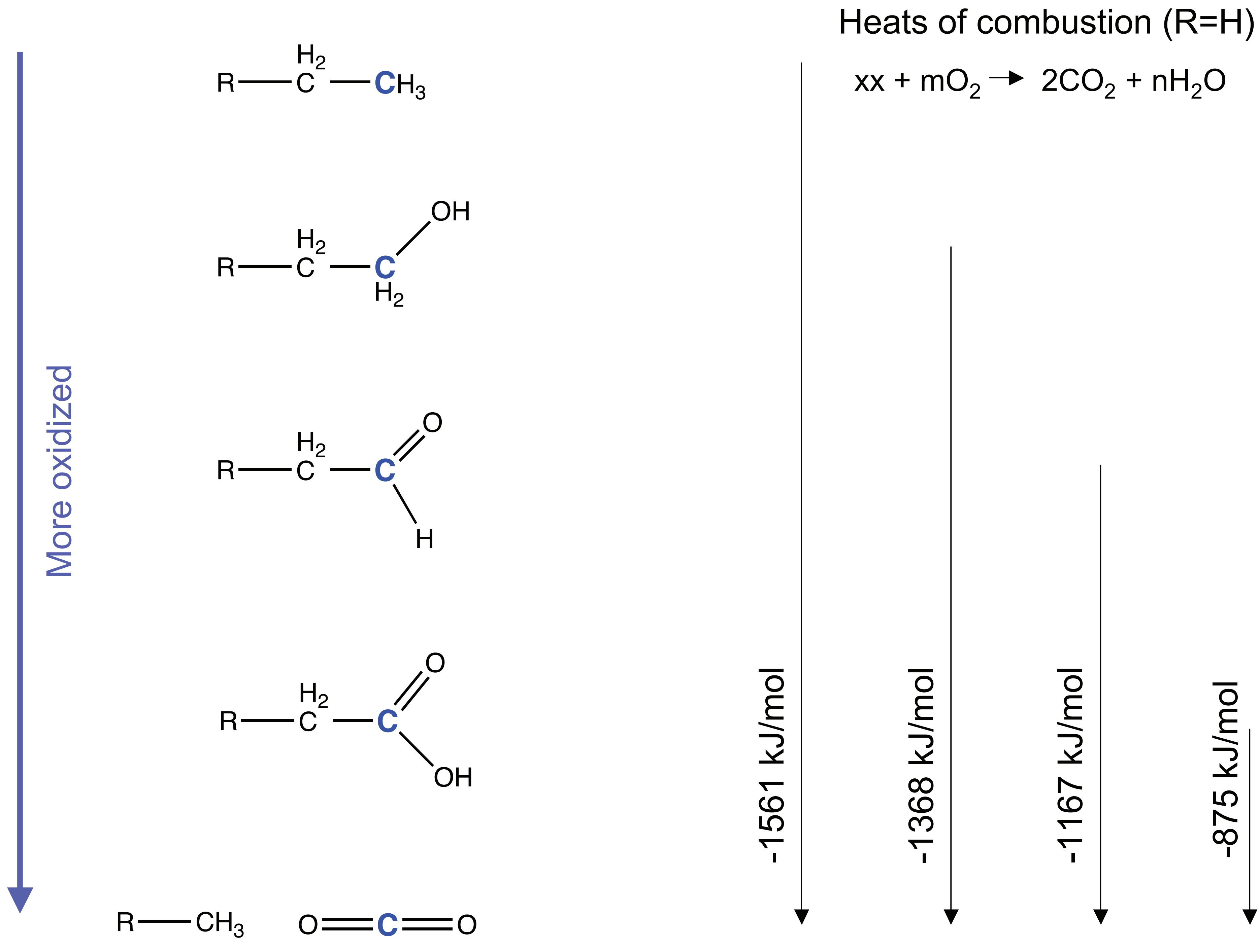

Heats of combustion (R=H)
$xx + mO_2 \rightarrow 2CO_2 + nH_2O$
More oxidized
-1561 kJ/mol
-1368 kJ/mol
-1167 kJ/mol
-875 kJ/mol

TABLE 13–4 **Standard Free-Energy Changes of Some Chemical Reactions at pH 7.0 and 25 °C (298 K)**

	$\Delta G'^{\circ}$	
Reaction type	*(kJ/mol)*	*(kcal/mol)*
Glycosides		
Maltose + H_2O ⟶ 2 glucose	−15.5	−3.7
Lactose + H_2O ⟶ glucose + galactose	−15.9	−3.8
Rearrangements		
Glucose 1-phosphate ⟶ glucose 6-phosphate	−7.3	−1.7
Fructose 6-phosphate ⟶ glucose 6-phosphate	−1.7	−0.4
Elimination of water		
Malate ⟶ fumarate + H_2O	3.1	0.8
Oxidations with molecular oxygen		
Glucose + $6O_2$ ⟶ $6CO_2$ + $6H_2O$	−2,840	−686
Palmitate + $23O_2$ ⟶ $16CO_2$ + $16H_2O$	−9,770	−2,338

TABLE 13–7 Standard Reduction Potentials of Some Biologically Important Half-Reactions, at pH 7.0 and 25 °C (298 K)

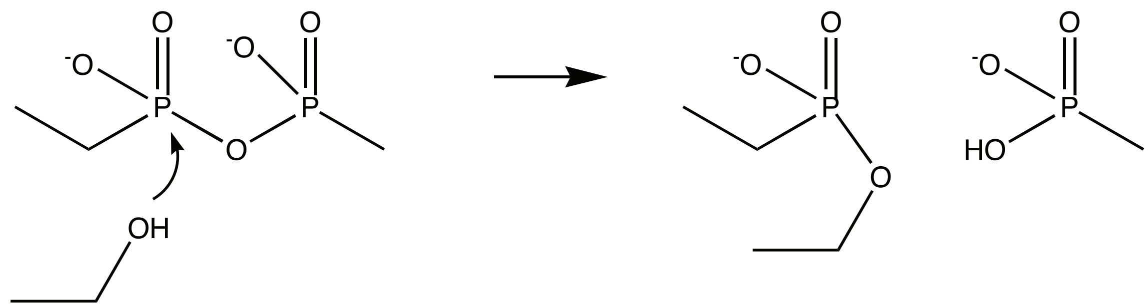
Half-reaction	*E′°* (*V*)
$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$	0.816
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.771
$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O$	0.421
Cytochrome *f* (Fe^{3+}) + e^- $\longrightarrow$ cytochrome *f* (Fe^{2+})	0.365
$Fe(CN)_6^{3-}$ (ferricyanide) + e^- $\longrightarrow$ $Fe(CN)_6^{4-}$	0.36
Cytochrome a_3 (Fe^{3+}) + e^- $\longrightarrow$ cytochrome a_3 (Fe^{2+})	0.35
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	0.295
Cytochrome *a* (Fe^{3+}) + e^- $\longrightarrow$ cytochrome *a* (Fe^{2+})	0.29
Cytochrome *c* (Fe^{3+}) + e^- $\longrightarrow$ cytochrome *c* (Fe^{2+})	0.254
Cytochrome c_1 (Fe^{3+}) + e^- $\longrightarrow$ cytochrome c_1 (Fe^{2+})	0.22
Cytochrome *b* (Fe^{3+}) + e^- $\longrightarrow$ cytochrome *b* (Fe^{2+})	0.077
Ubiquinone + $2H^+ + 2e^-$ $\longrightarrow$ ubiquinol + H_2	0.045
Fumarate^{2-} + $2H^+ + 2e^-$ $\longrightarrow$ succinate^{2-}	0.031
$2H^+ + 2e^- \longrightarrow H_2$ (at standard conditions, pH 0)	0.000

Source: Data mostly from Loach, P.A. (1976) In *Handbook of Biochemistry and Molecular Biology*, 3rd edn (Fasman, G.D., ed.), *Physical and Chemical Data*, Vol. I, pp. 122–130, CRC Press, Boca Raton, FL.

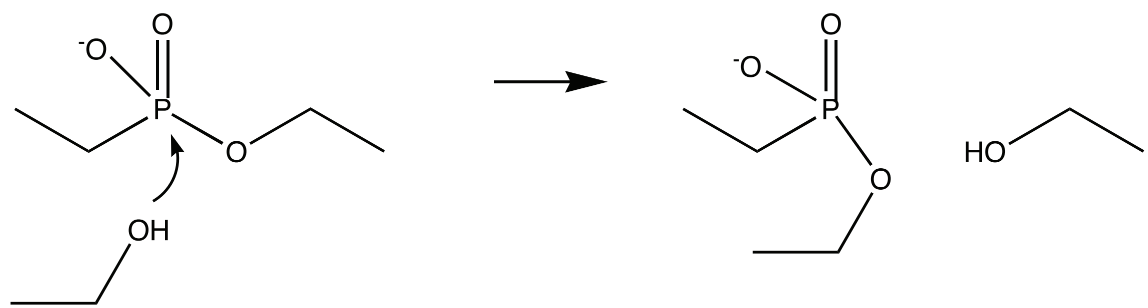
* This is the value for free FAD; FAD bound to a specific flavoprotein (for example succinate dehydrogenase) has a different *E′°* that depends on its protein environments.

Which reaction is most favorable?

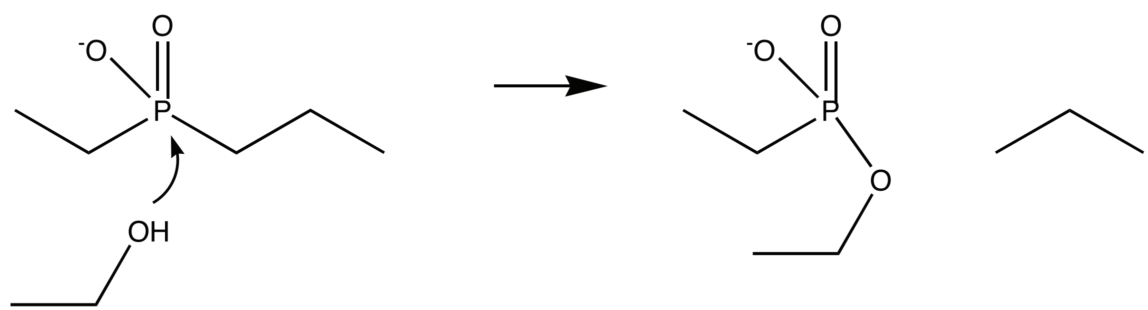
1)



2)

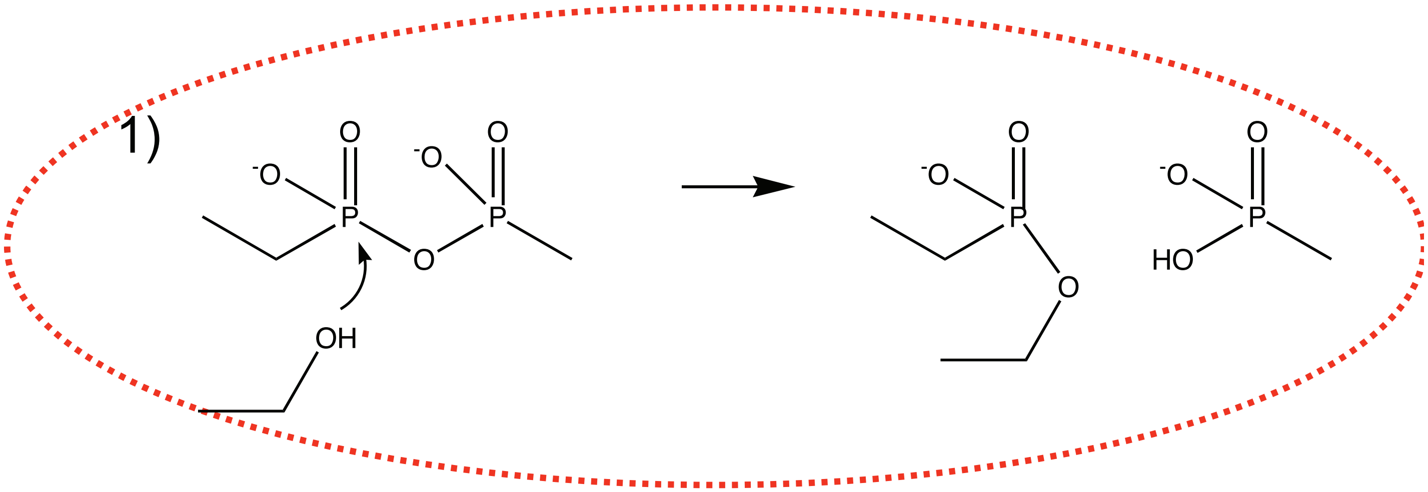


3)

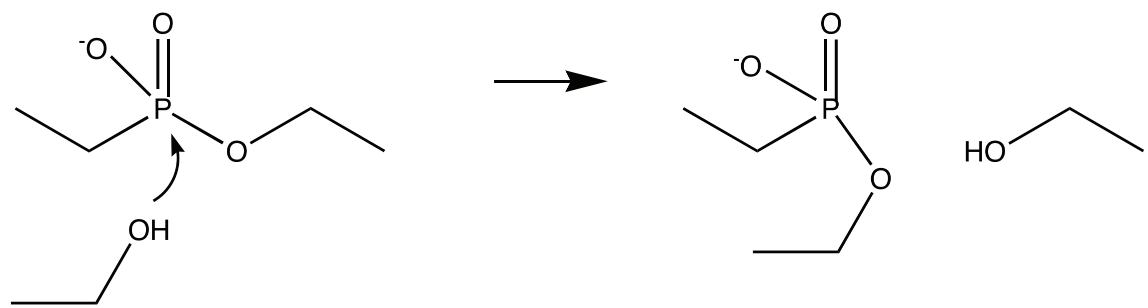


Which reaction is most favorable?

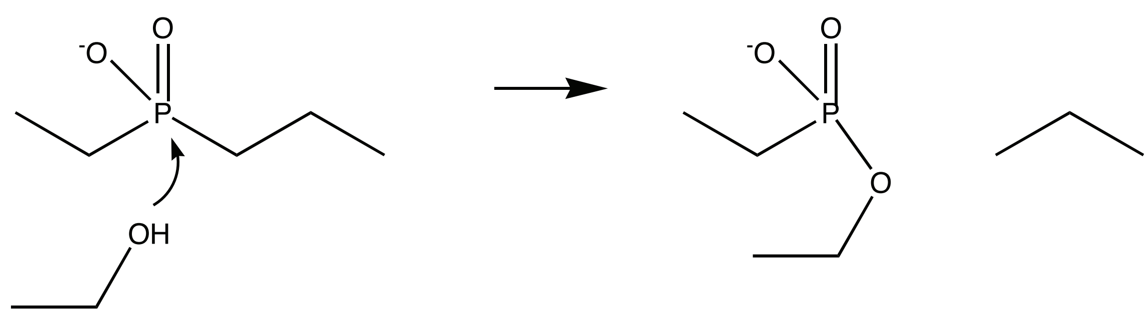
1)



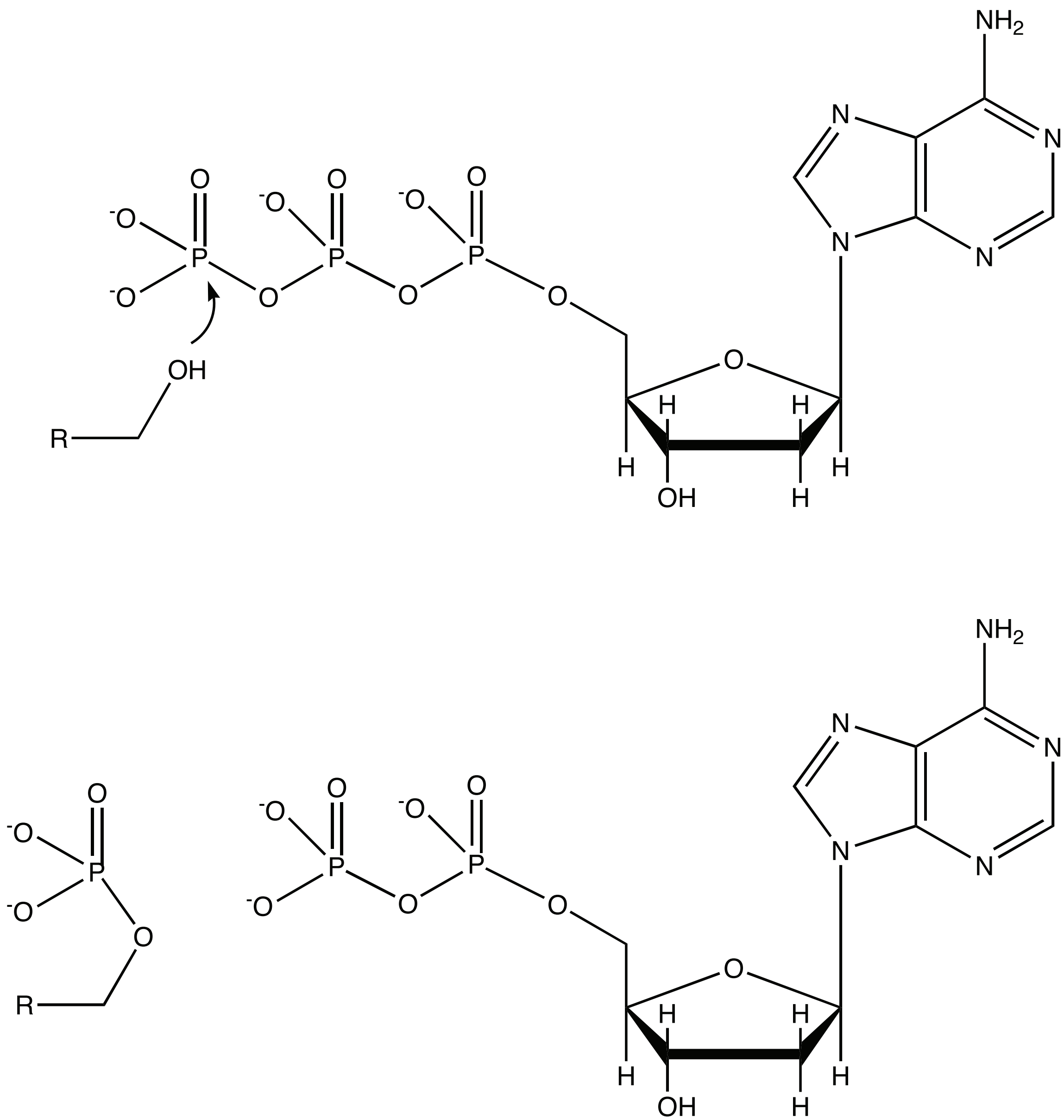
2)



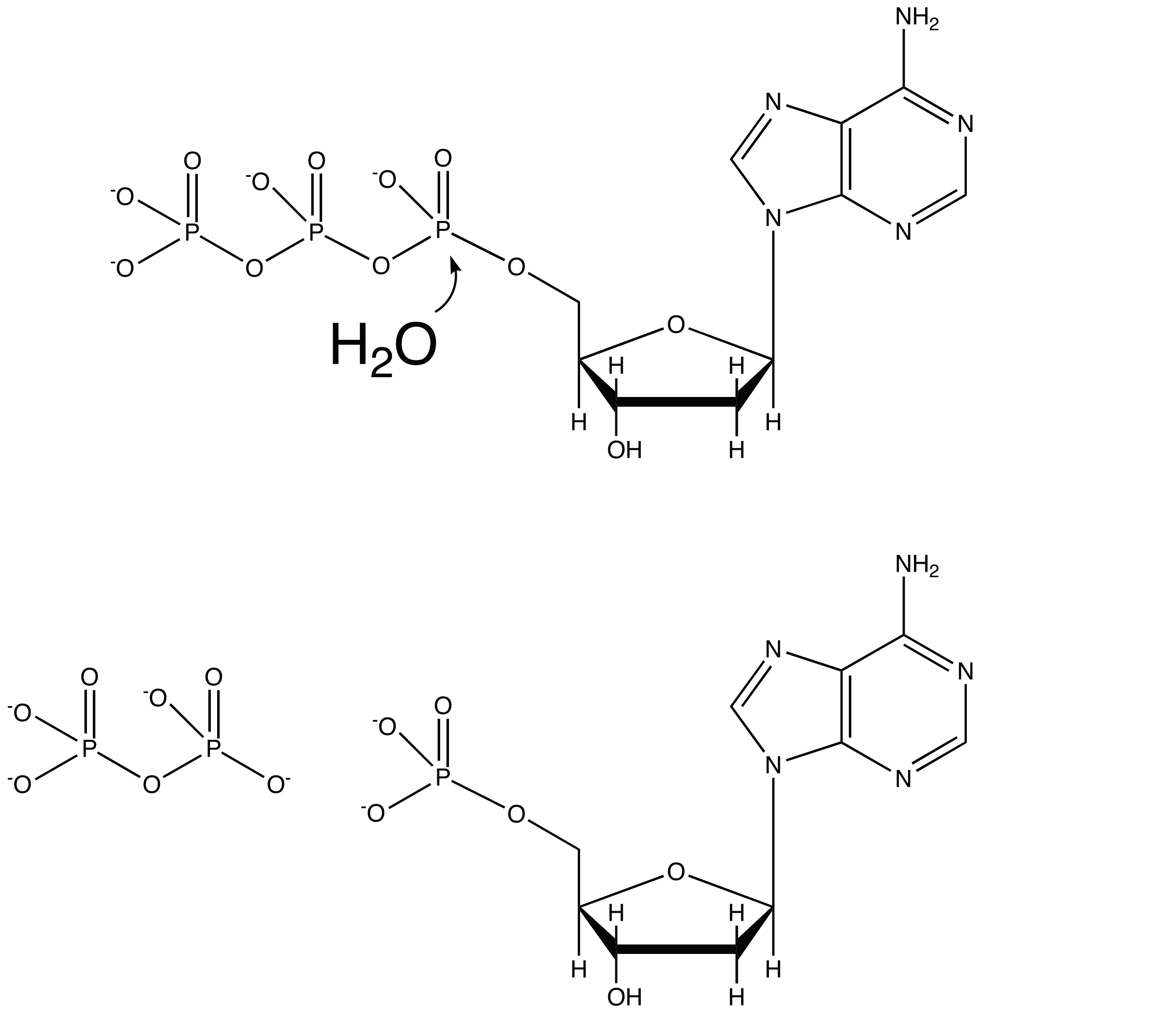
3)



ATP - can “phosphorylate” alchohols



ATP - hydrolysis VERY favorable



ATP - Two uses

Phosphorylate things

Hydrolysis coupled to unfavorable reactions

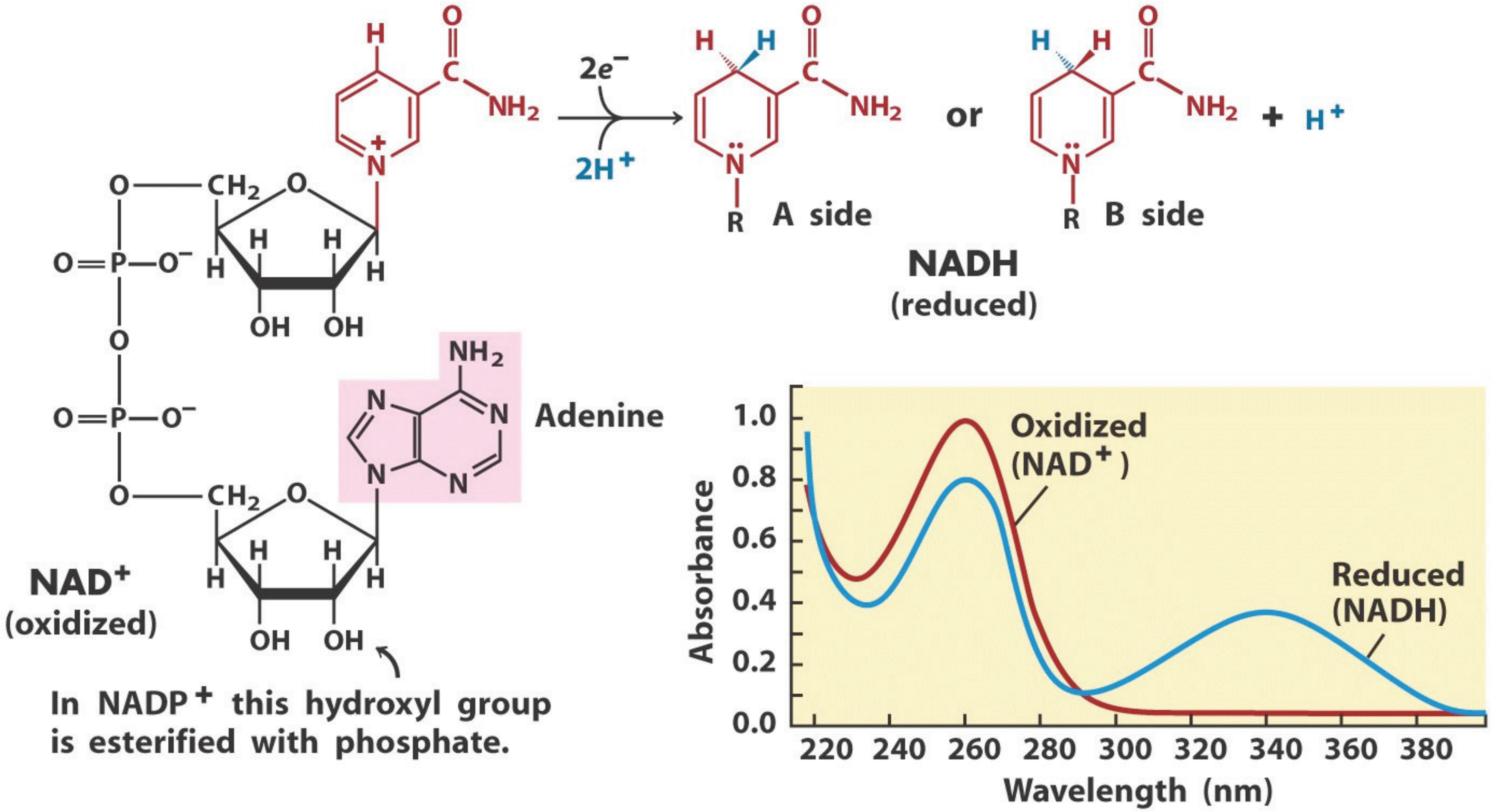
Oh, and it's a part of RNA and DNA

TABLE 13–7 **Standard Reduction Potentials of Some Biologically Important Half-Reactions, at pH 7.0 and 25 °C (298 K)**

Half-reaction	E'° *(V)*
$2H^+ + 2e^- \longrightarrow H_2$ (at standard conditions, pH 0)	0.000
Crotonyl-CoA $+ 2H^+ + 2e^- \longrightarrow$ butyryl-CoA	−0.015
Oxaloacetate^{2-} $+ 2H^+ + 2e^- \longrightarrow$ malate^{2-}	−0.166
Pyruvate$^-$ $+ 2H^+ + 2e^- \longrightarrow$ lactate$^-$	−0.185
Acetaldehyde $+ 2H^+ + 2e^- \longrightarrow$ ethanol	−0.197
$FAD + 2H^+ + 2e^- \longrightarrow FADH_2$	−0.219*
Glutathione $+ 2H^+ + 2e^- \longrightarrow$ 2 reduced glutathione	−0.23
$S + 2H^+ + 2e^- \longrightarrow H_2S$	−0.243
Lipoic acid $+ 2H^+ + 2e^- \longrightarrow$ dihydrolipoic acid	−0.29
$NAD^+ + H^+ + 2e^- \longrightarrow NADH$	−0.320
$NADP^+ + H^+ + 2e^- \longrightarrow NADPH$	−0.324
Acetoacetate $+ 2H^+ + 2e^- \longrightarrow$ β-hydroxybutyrate	−0.346
α-Ketoglutarate $+ CO_2 + 2H^+ + 2e^- \longrightarrow$ isocitrate	−0.38
$2H^+ + 2e^- \longrightarrow H_2$ (at pH 7)	−0.414
Ferredoxin (Fe^{3+}) $+ e^- \longrightarrow$ ferredoxin (Fe^{2+})	−0.432

Source: Data mostly from Loach, P.A. (1976) In *Handbook of Biochemistry and Molecular Biology*, 3rd edn (Fasman, G.D., ed.), *Physical and Chemical Data*, Vol. I, pp. 122–130, CRC Press, Boca Raton, FL.

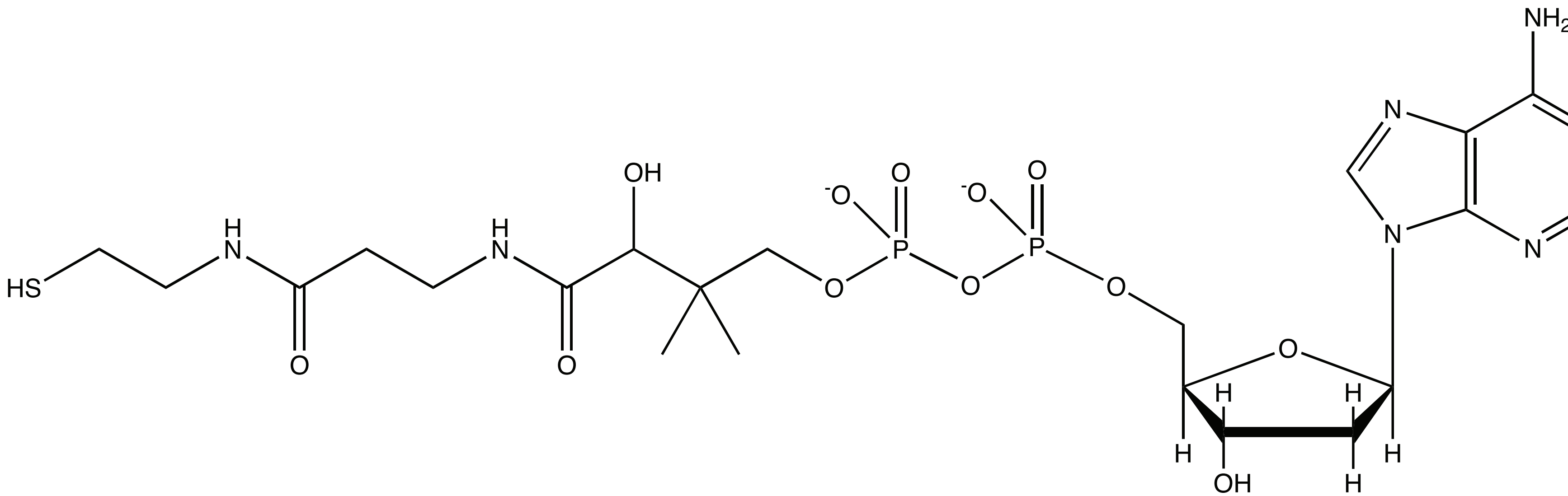
* This is the value for free FAD; FAD bound to a specific flavoprotein (for example succinate dehydrogenase) has a different E'° that depends on its protein environments.



NAD+
(oxidized)
Adenine
2e−
2H+
A side
or
B side
+ H+
NADH
(reduced)
In NADP+ this hydroxyl group is esterified with phosphate.
Absorbance
Wavelength (nm)
Oxidized
(NAD+)
Reduced
(NADH)

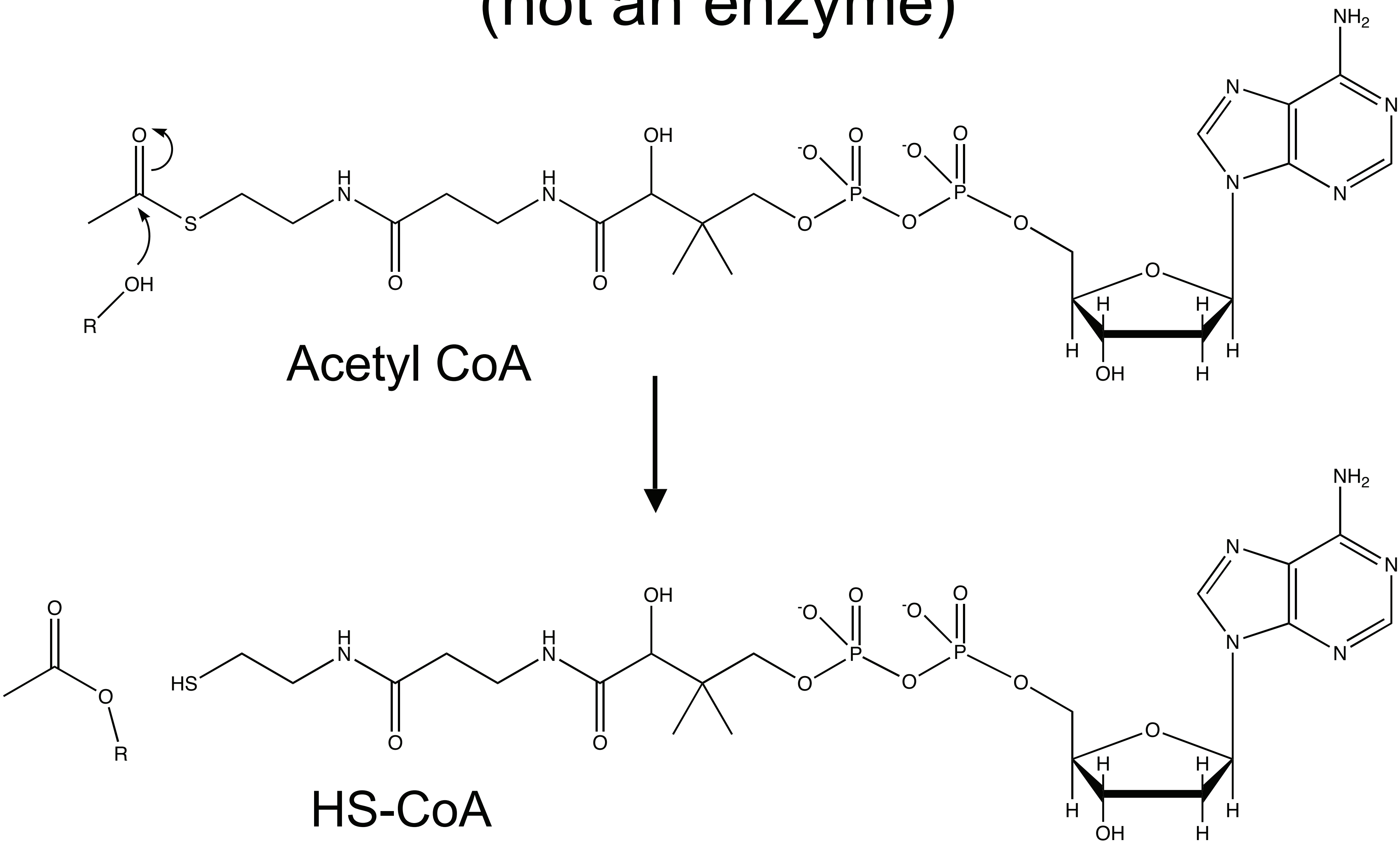
Coenzyme A

(not an enzyme)



Coenzyme A

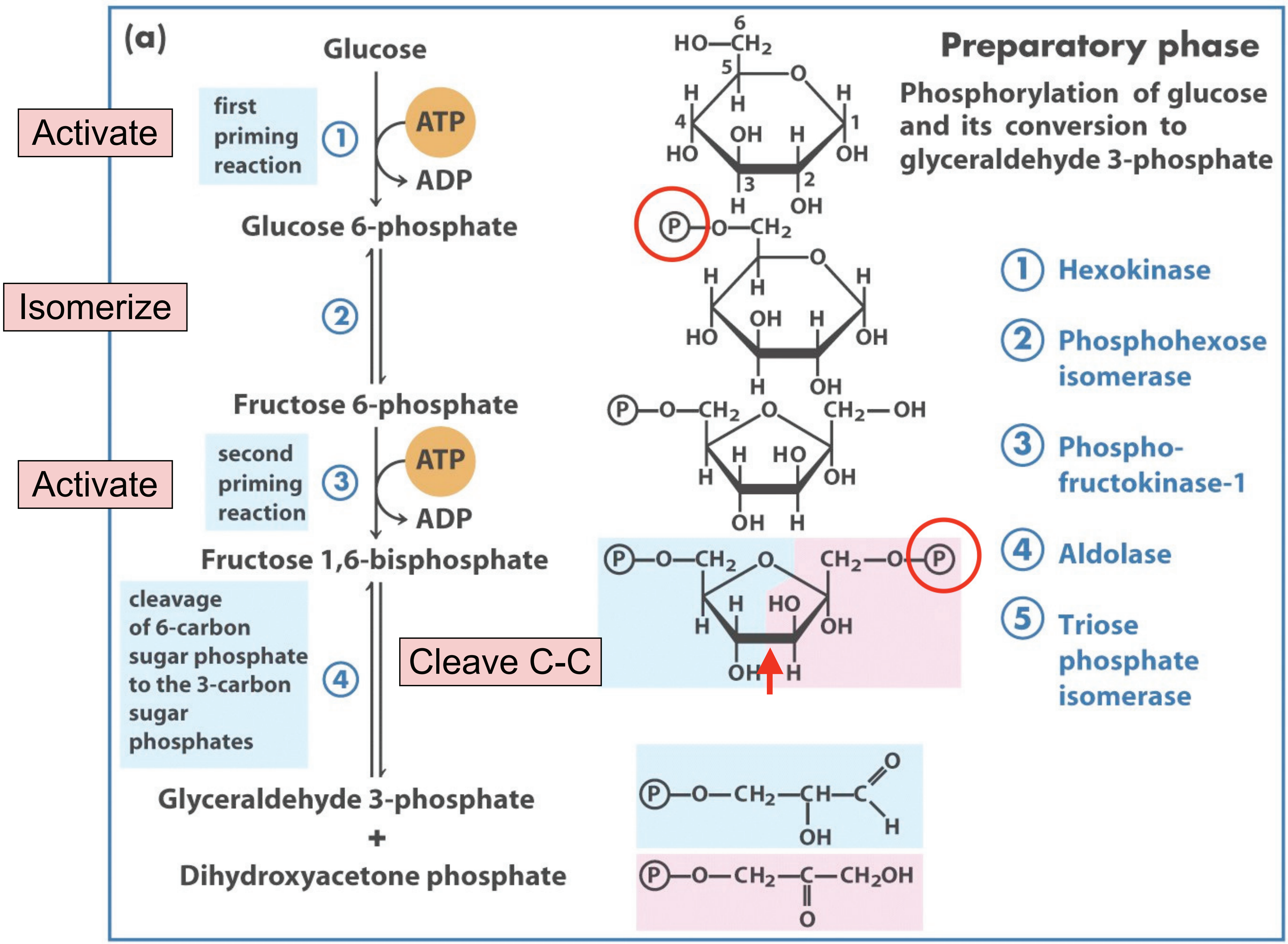
(not an enzyme)



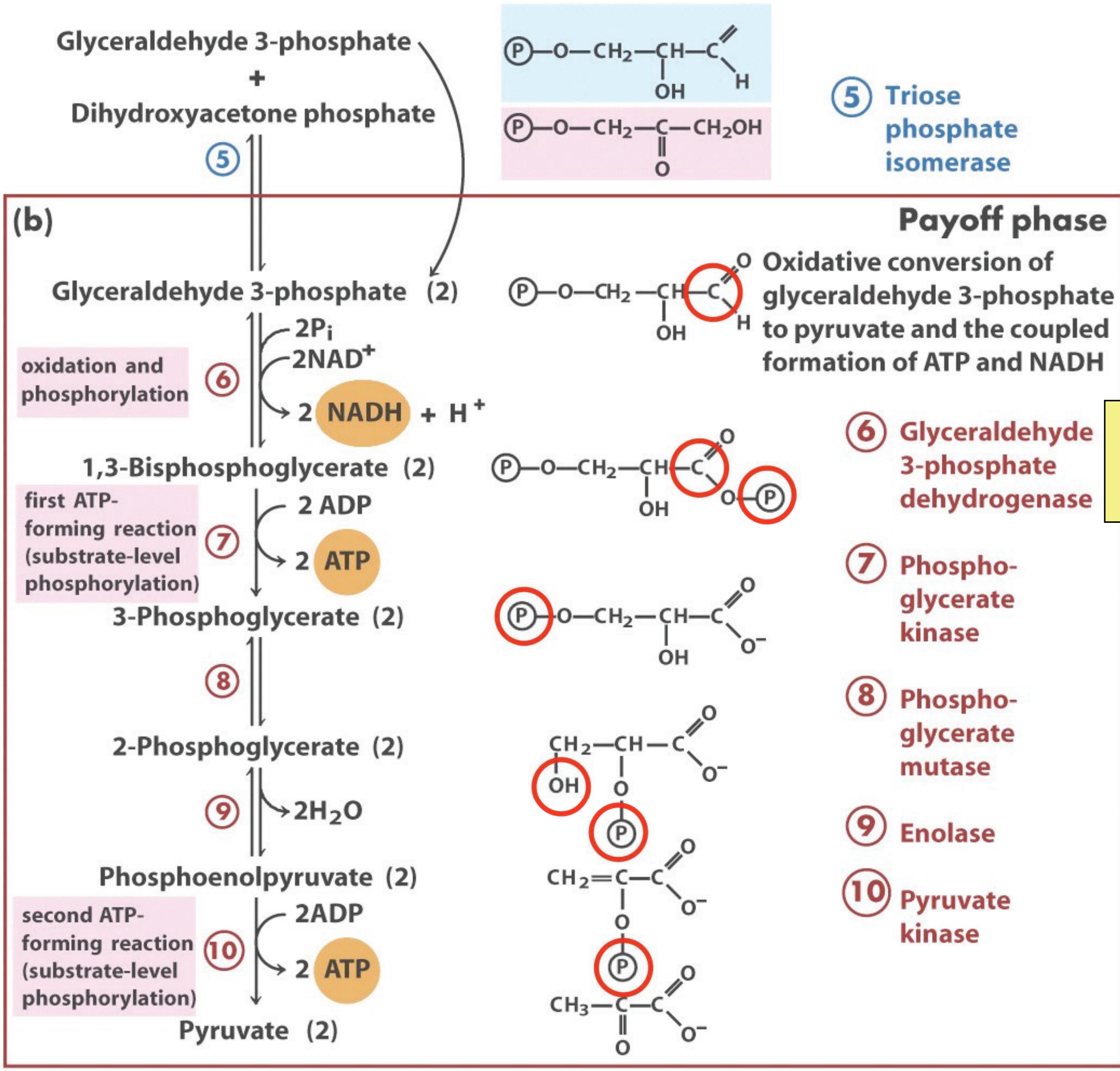
Glycolysis

Combustion ("burning") of sugars (carbohydrates)

Oxidations with molecular oxygen	ΔG°' (kJ/mol)	(kcal/mol)
Glucose + $6O_2 \longrightarrow 6CO_2 + 6H_2O$	−2,840	−686
Palmitate + $23O_2 \longrightarrow 16CO_2 + 16H_2O$	−9,770	−2,338



Activate
Isomerize
Activate
Cleave C-C
(a)
Preparatory phase
Phosphorylation of glucose and its conversion to glyceraldehyde 3-phosphate
Glucose
first priming reaction
1
ATP
ADP
Glucose 6-phosphate
2
Fructose 6-phosphate
second priming reaction
3
ATP
ADP
Fructose 1,6-bisphosphate
cleavage of 6-carbon sugar phosphate to the 3-carbon sugar phosphates
4
Glyceraldehyde 3-phosphate
+
Dihydroxyacetone phosphate
1 Hexokinase
2 Phosphohexose isomerase
3 Phospho-fructokinase-1
4 Aldolase
5 Triose phosphate isomerase



Oxidize and phosphorylate

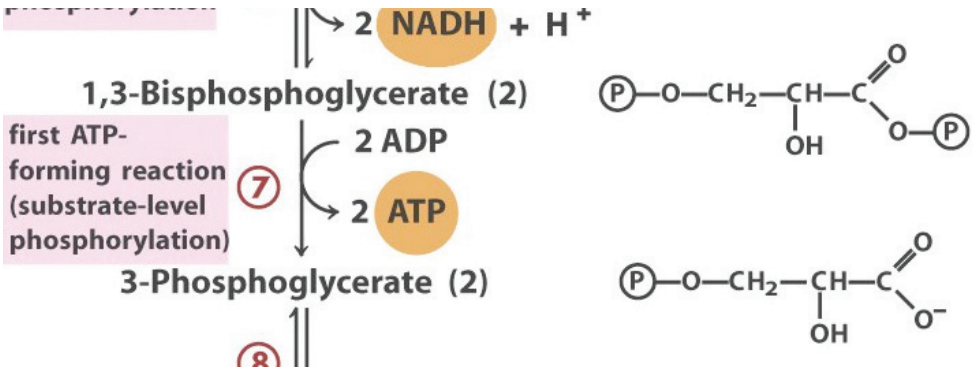
Phospho-anhydride is High Energy

Transfer P to ADP

Intramolec xfer of P

Dehydrate enol ester

Transfer P to ADP



This time,

reaction of 1,3-bisphosphoglycerate to 3-phosphoglycerate is more favorable than hydrolysis of ATP

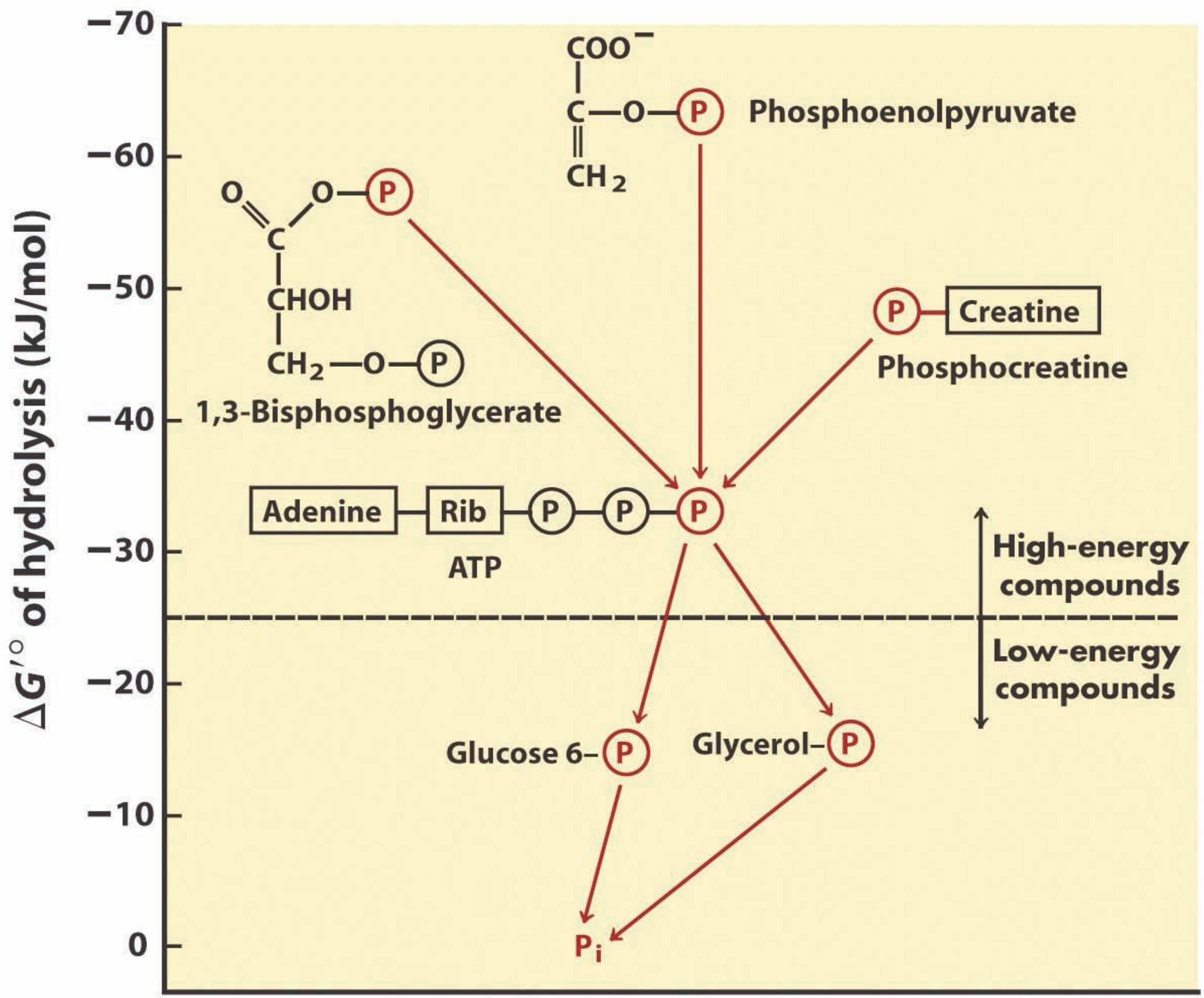
So the reaction drives hydrolysis *backwards* - makes ATP from ADP

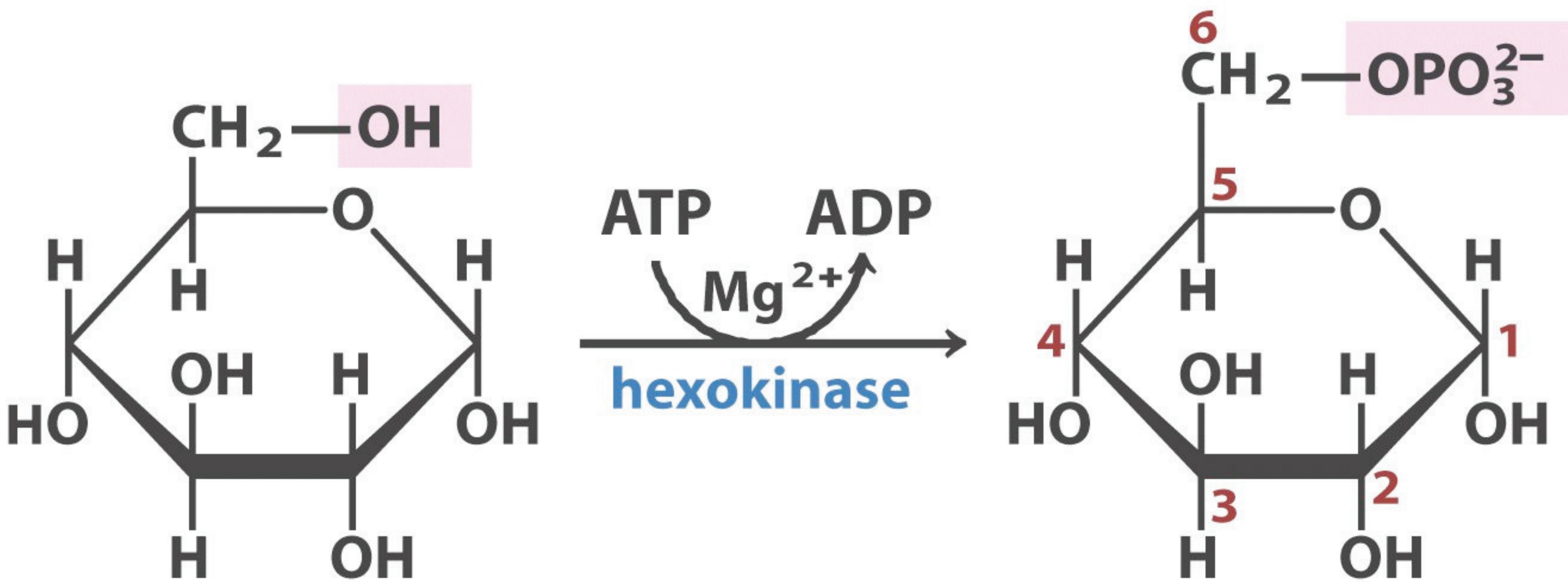
Energy has been STORED.

TABLE 13–6 Standard Free Energies of Hydrolysis of Some Phosphorylated Compounds and Acetyl-CoA (a Thioester)

	$\Delta G'^{\circ}$ (kJ/mol)	$\Delta G'^{\circ}$ (kcal/mol)
Phosphoenolpyruvate	−61.9	−14.8
1,3-bisphosphoglycerate (→ 3-phosphoglycerate + P_i)	−49.3	−11.8
Phosphocreatine	−43.0	−10.3
ADP (→ AMP + P_i)	−32.8	−7.8
ATP (→ ADP + P_i)	−30.5	−7.3
ATP (→ AMP + PP_i)	−45.6	−10.9
AMP (→ adenosine + P_i)	−14.2	−3.4
PP_i (→ 2P_i)	−19.2	−4.0
Glucose 1-phosphate	−20.9	−5.0
Fructose 6-phosphate	−15.9	−3.8
Glucose 6-phosphate	−13.8	−3.3
Glycerol 1-phosphate	−9.2	−2.2
Acetyl-CoA	−31.4	−7.5

Source: Data mostly from Jencks, W.P. (1976) in *Handbook of Biochemistry and Molecular Biology,* 3rd edn (Fasman, G.D., ed.), *Physical and Chemical Data,* Vol. I, pp. 296–304, CRC Press, Boca Raton, FL. The value for the free energy of hydrolysis of PP_i is from Frey, P.A. & Arabshahi, A. (1995) Standard free-energy change for the hydrolysis of the α–β-phosphoanhydride bridge in ATP. *Biochemistry* **34,** 11,307–11,310.

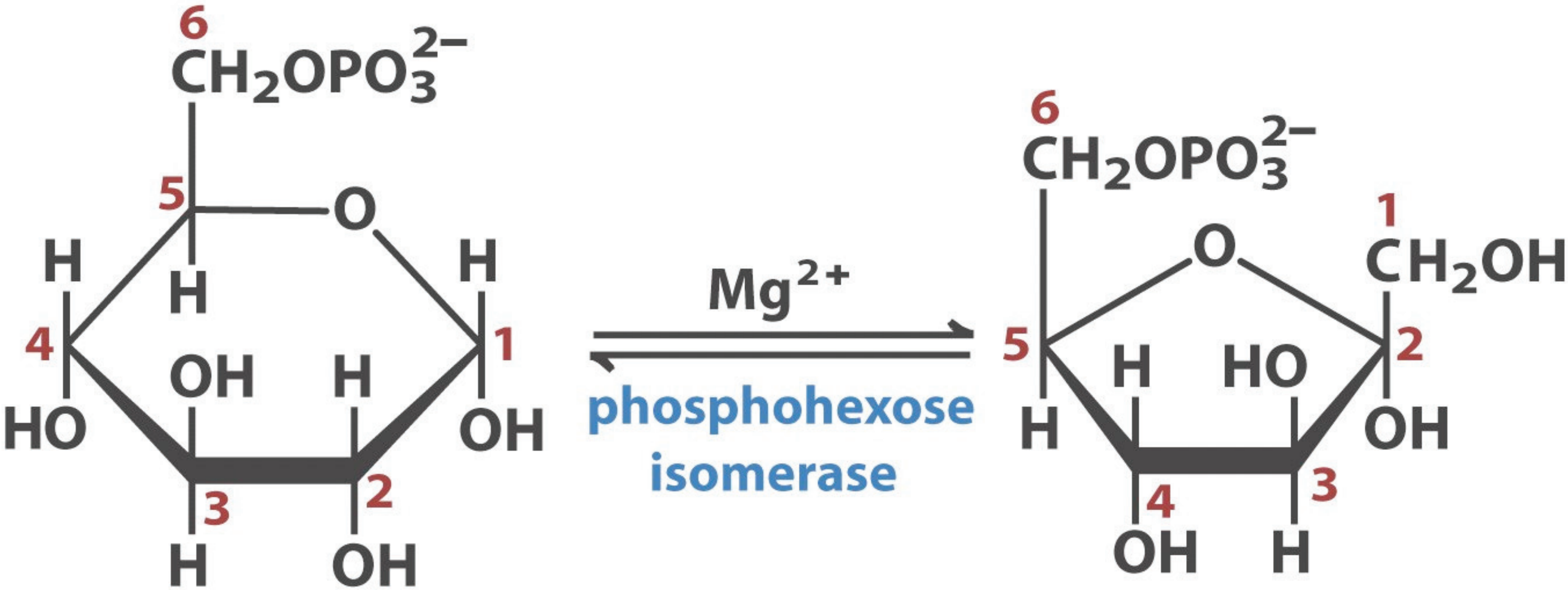

ΔG′° of hydrolysis (kJ/mol)
−70
−60
−50
−40
−30
−20
−10
0
COO⁻
C—O—P
CH 2
Phosphoenolpyruvate
O
O—P
C
CHOH
CH2—O—P
1,3-Bisphosphoglycerate
P—Creatine
Phosphocreatine
Adenine
Rib
P
P
P
ATP
High-energy compounds
Low-energy compounds
Glucose 6–P
Glycerol–P
Pi



Glucose

Glucose 6-phosphate

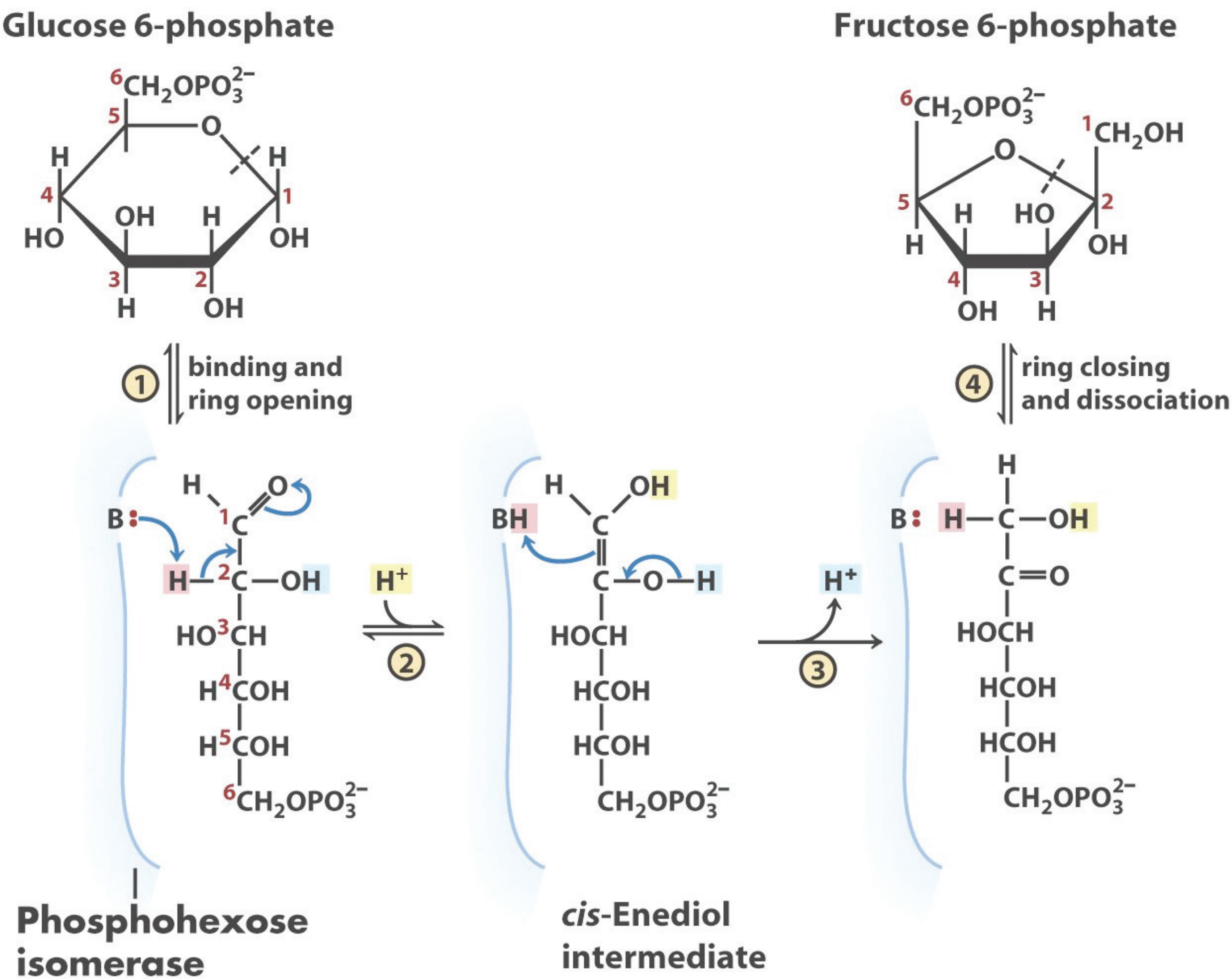
$$\Delta G'^{\circ} = -16.7\ \text{kJ/mol}$$

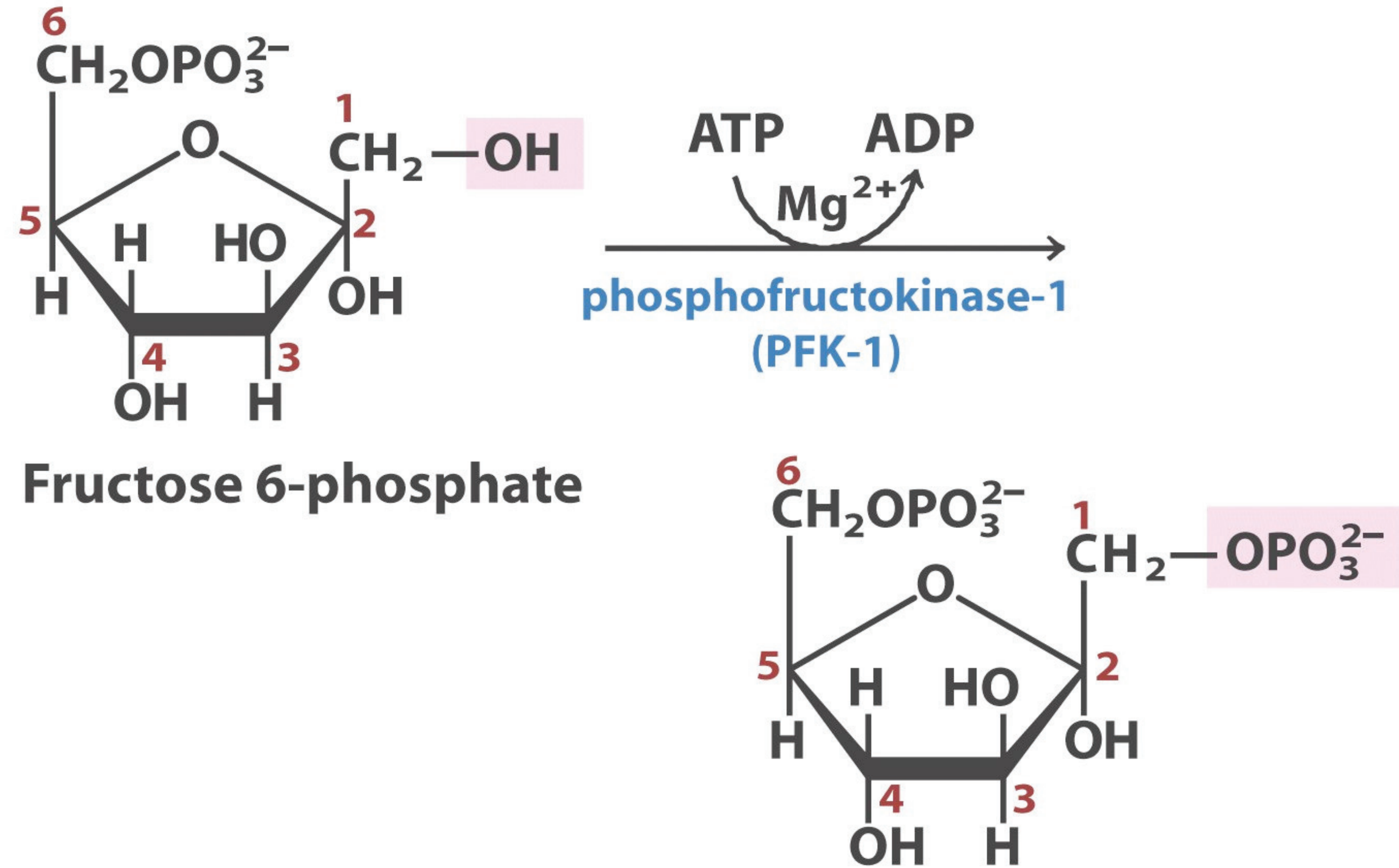


Glucose 6-phosphate

Fructose 6-phosphate

$\Delta G'^{\circ} = 1.7$ kJ/mol

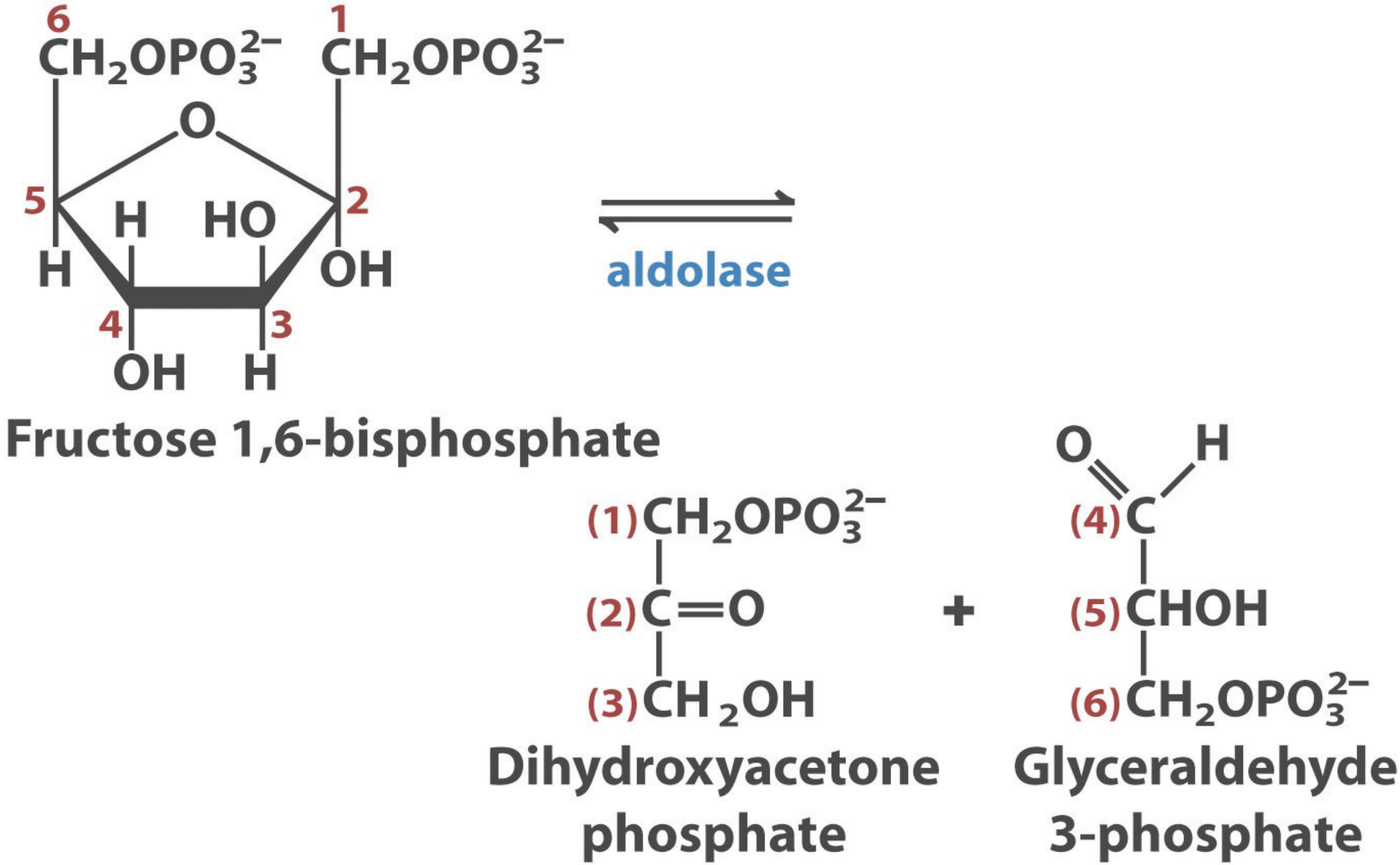

Glucose 6-phosphate
Fructose 6-phosphate
binding and ring opening
ring closing and dissociation
B:
BH
H+
cis-Enediol intermediate
Phosphohexose isomerase



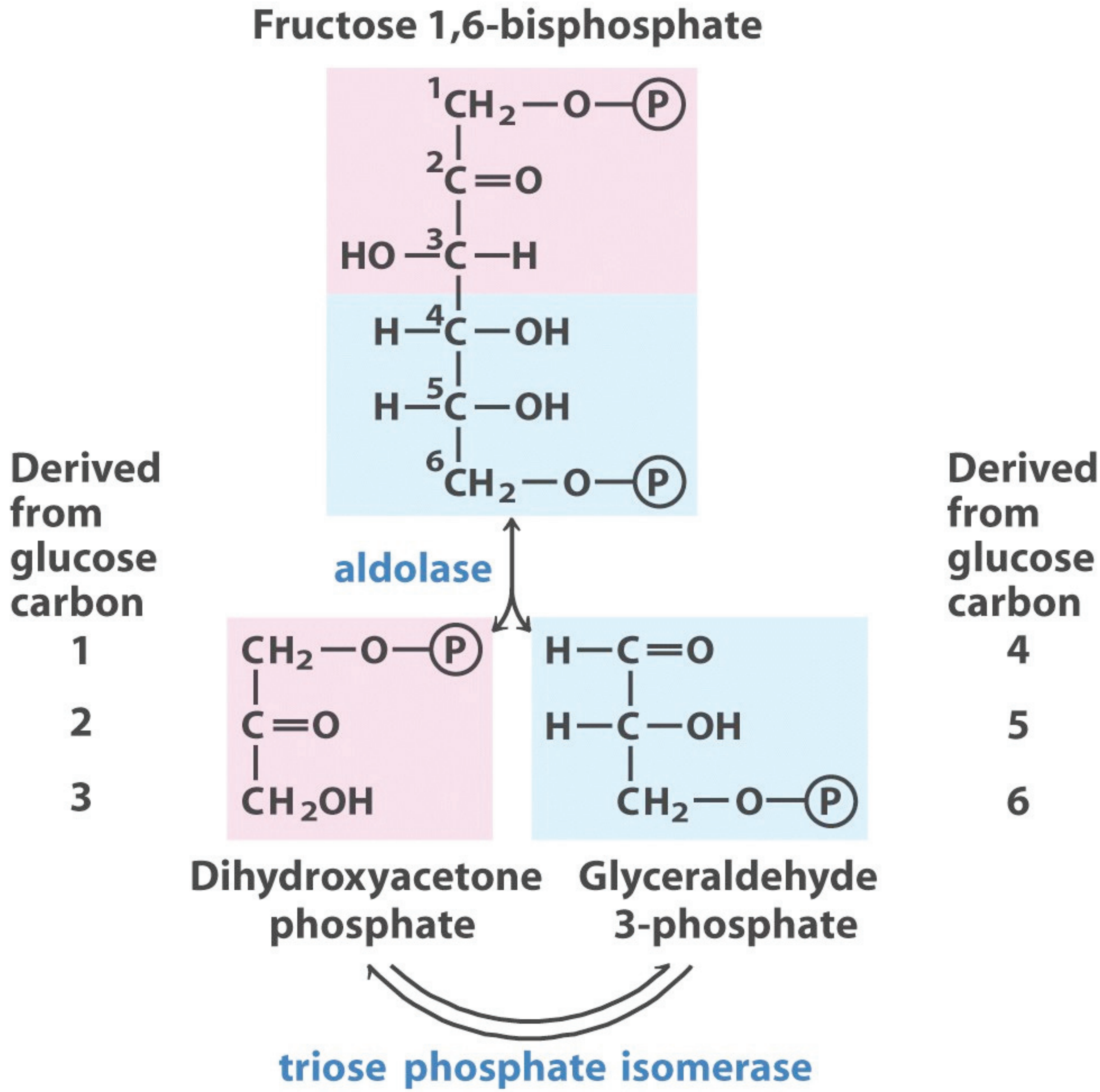
Fructose 6-phosphate

Fructose 1,6-bisphosphate

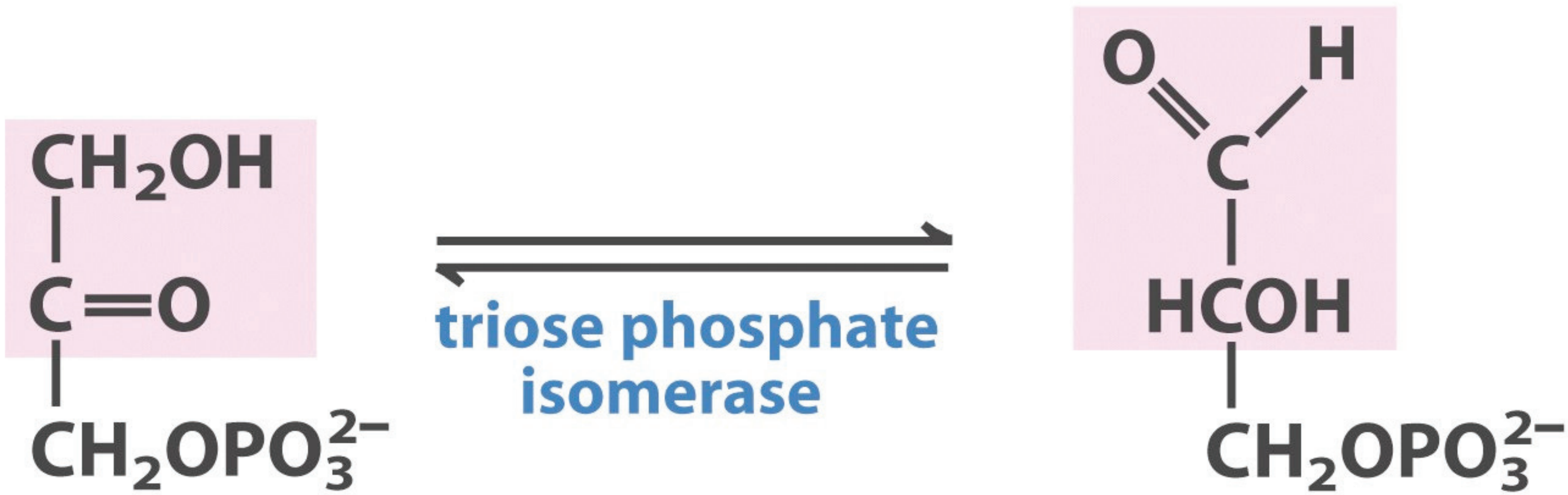
$\Delta G'^{\circ} = -14.2 \text{ kJ/mol}$



$$\Delta G'^{\circ} = 23.8 \text{ kJ/mol}$$



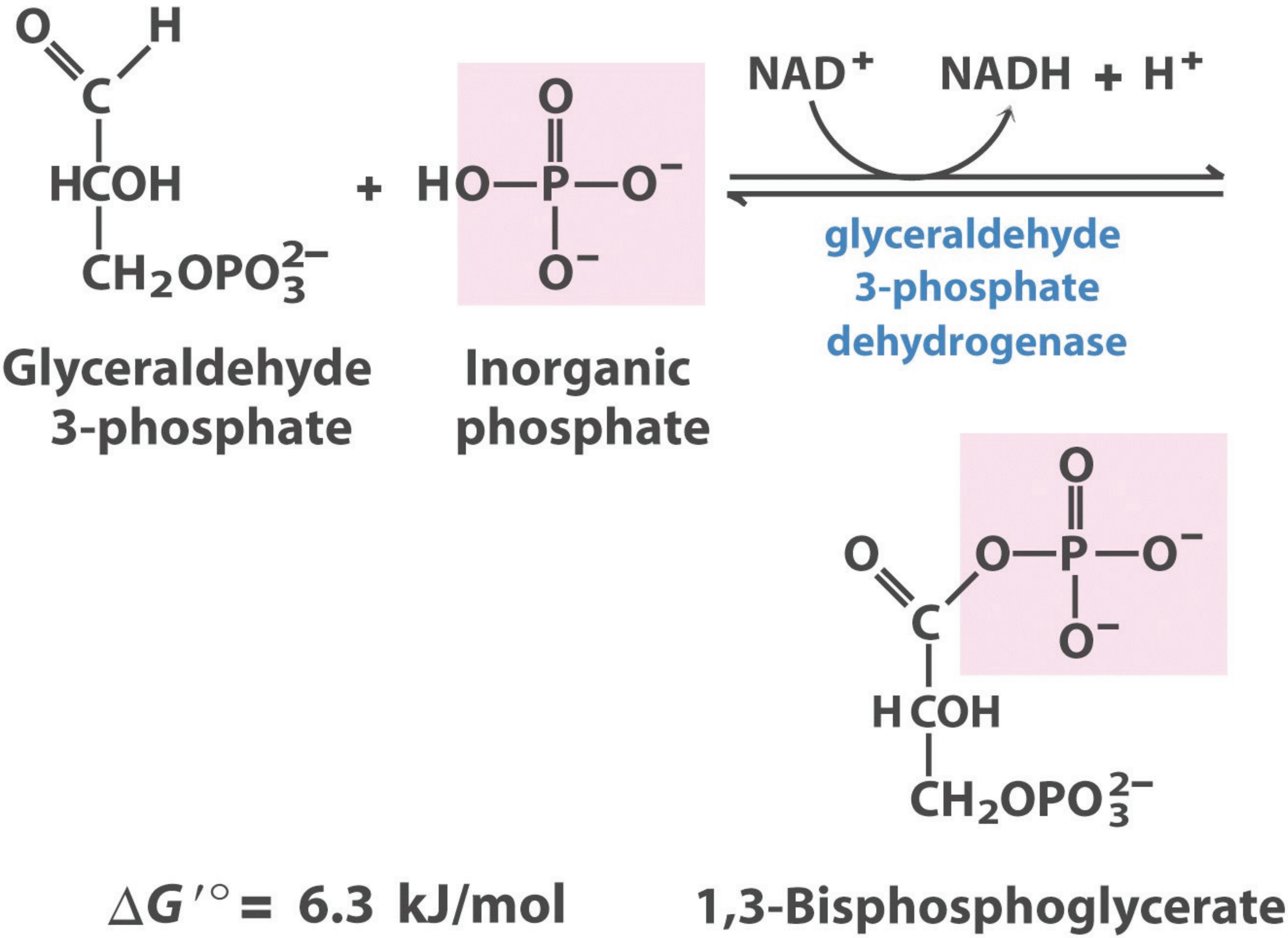
Fructose 1,6-bisphosphate
Derived from glucose carbon
aldolase
Derived from glucose carbon
1
2
3
4
5
6
Dihydroxyacetone phosphate
Glyceraldehyde 3-phosphate
triose phosphate isomerase

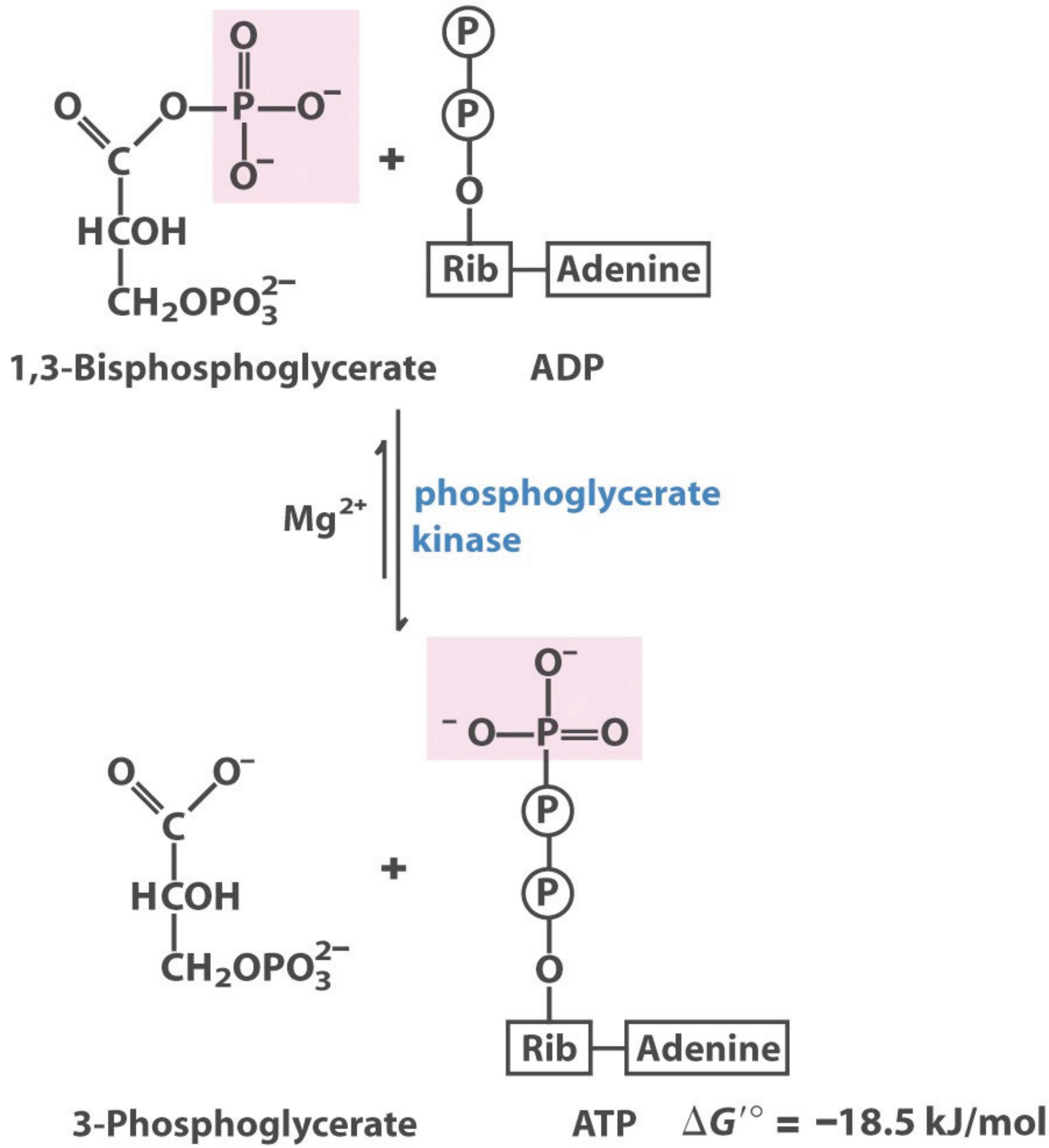


Dihydroxyacetone phosphate

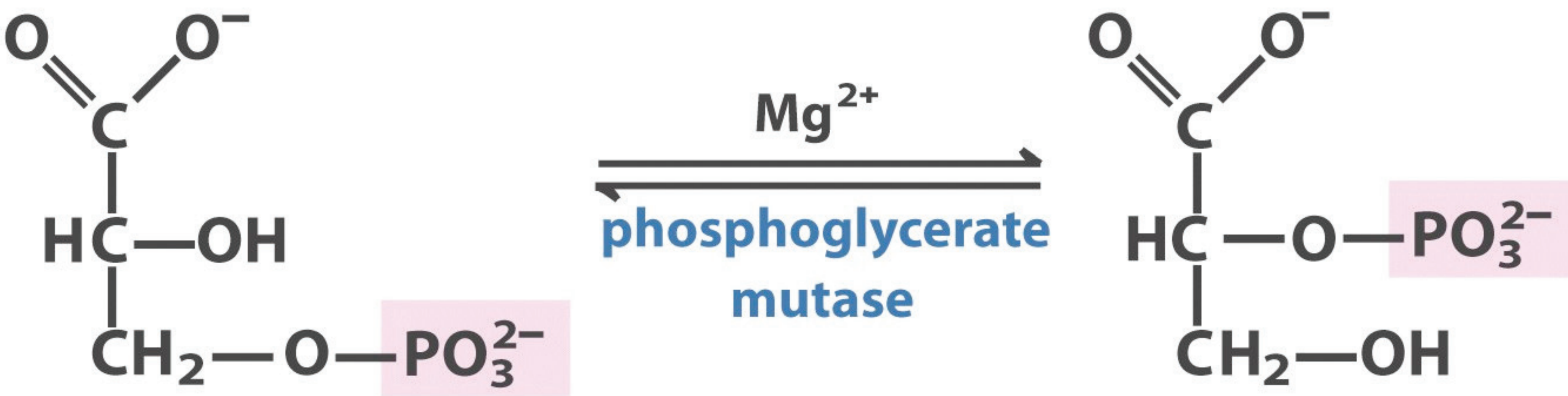
Glyceraldehyde 3-phosphate

$\Delta G'^{\circ} = 7.5\ \text{kJ/mol}$


NAD+
NADH + H+
glyceraldehyde 3-phosphate dehydrogenase
Glyceraldehyde 3-phosphate
Inorganic phosphate
1,3-Bisphosphoglycerate
ΔG′° = 6.3 kJ/mol



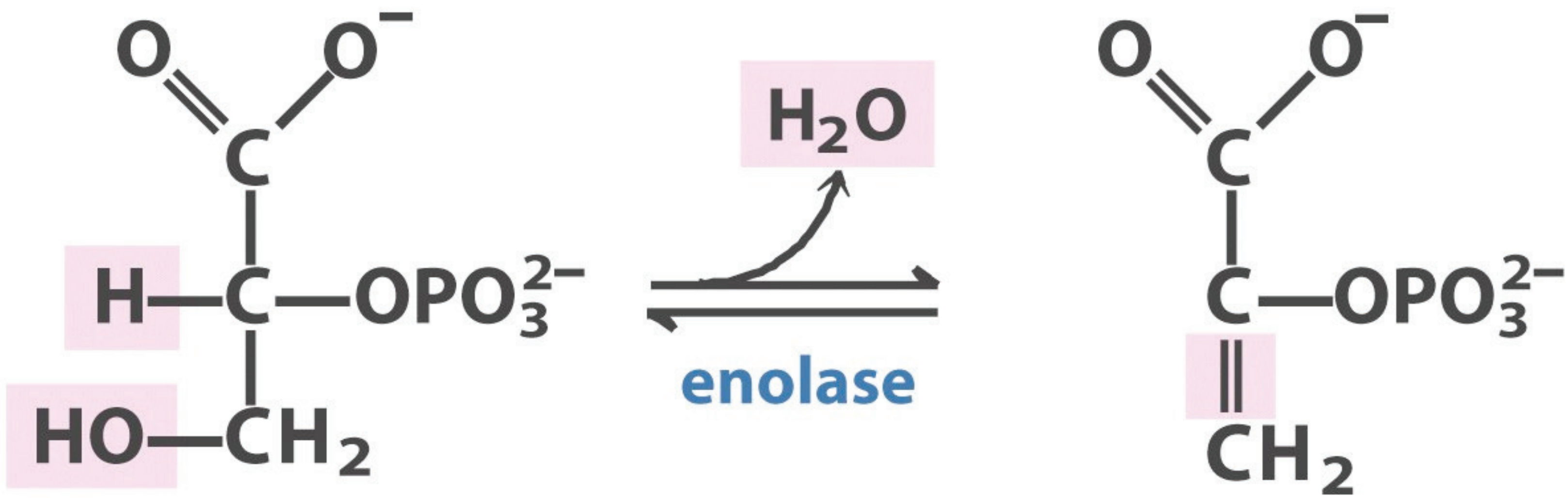
1,3-Bisphosphoglycerate
ADP
Rib
Adenine
Mg2+
phosphoglycerate kinase
3-Phosphoglycerate
ATP
ΔG′° = −18.5 kJ/mol



3-Phosphoglycerate

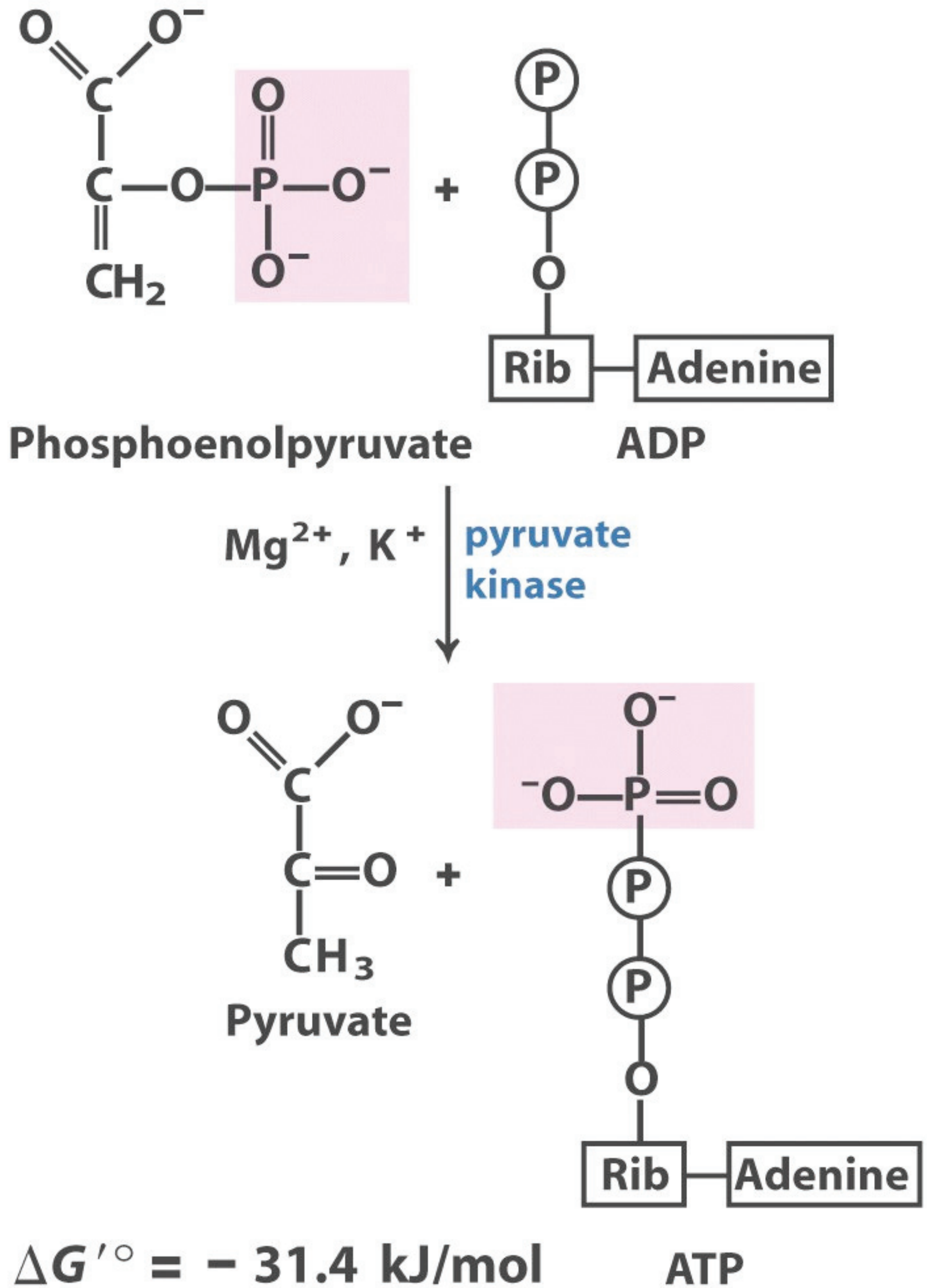
2-Phosphoglycerate

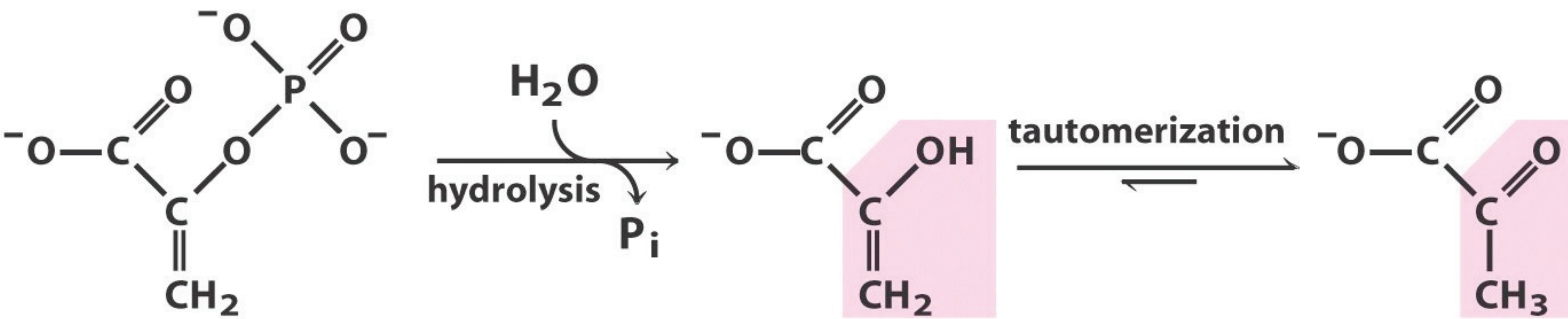
$\Delta G'^{\circ} = 4.4\ \text{kJ/mol}$



2-Phosphoglycerate **Phosphoenolpyruvate**

$$\Delta G'^{\circ} = 7.5 \text{ kJ/mol}$$


Phosphoenolpyruvate
ADP
Mg2+, K+
pyruvate kinase
Pyruvate
ATP
Rib
Adenine
ΔG′° = − 31.4 kJ/mol

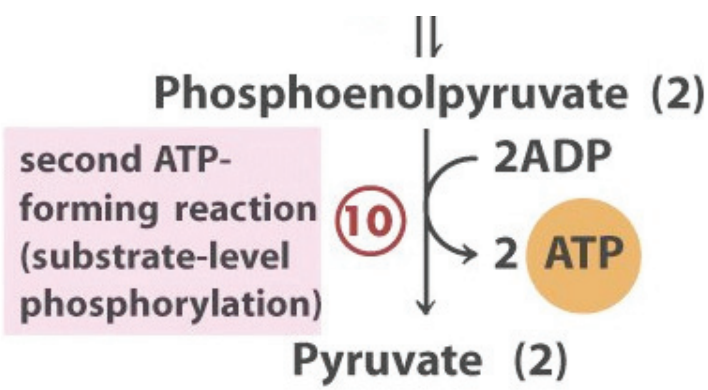


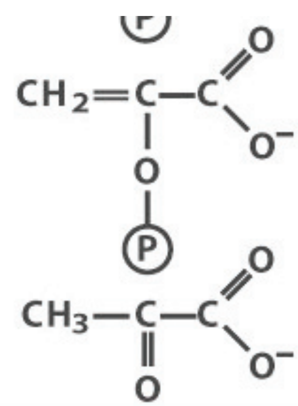
PEP

Pyruvate (enol form)

Pyruvate (keto form)

$$PEP^{3-} + H_2O \longrightarrow pyruvate^{-} + P_i^{2-}$$
$$\Delta G'^{\circ} = -61.9\ kJ/mol$$





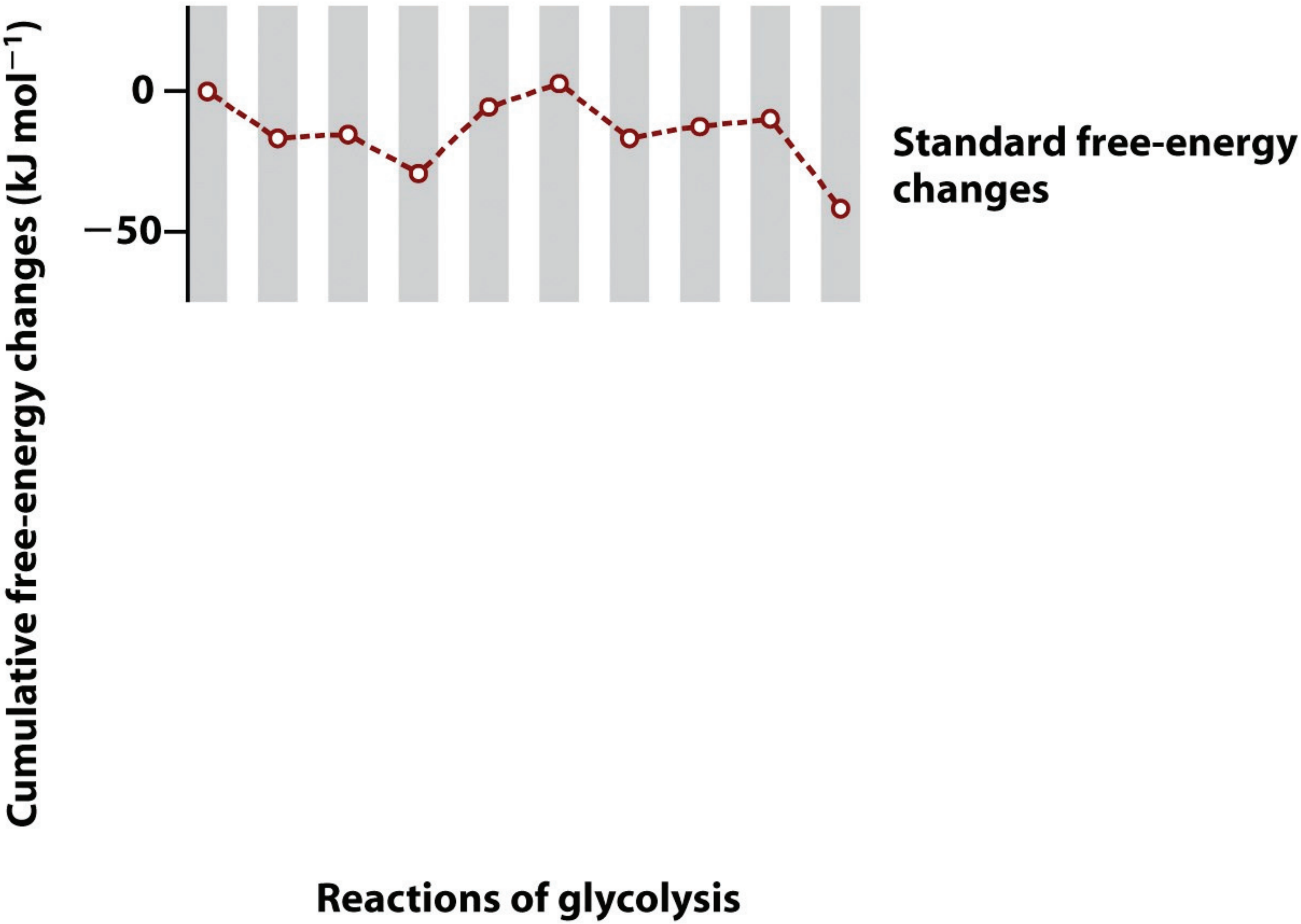


Figure 11-11 Principles of Biochemistry, 4/e

TABLE 14–2 Free-Energy Changes of Glycolytic Reactions in Erythrocytes

Glycolytic reaction step	$\Delta G'^{\circ}$ *(kJ/mol)*	ΔG *(kJ/mol)*
① Glucose + ATP ⟶ glucose 6-phosphate + ADP	−16.7	−33.4
② Glucose 6-phosphate ⇌ fructose 6-phosphate	1.7	0 to 25
③ Fructose 6-phosphate + ATP ⟶ fructose 1,6-bisphosphate + ADP	−14.2	−22.2
④ Fructose 1,6-bisphosphate ⇌ dihydroxyacetone phosphate + glyceraldehyde 3-phosphate	23.8	0 to −6
⑤ Dihydroxyacetone phosphate ⇌ glyceraldehyde 3-phosphate	7.5	0 to 4
⑥ Glyceraldehyde 3-phosphate + P_i + NAD^+ ⇌ 1,3-bisphosphoglycerate + NADH + H^+	6.3	−2 to 2
⑦ 1,3-Bisphosphoglycerate + ADP ⇌ 3-phosphoglycerate + ATP	−18.8	0 to 2
⑧ 3-Phosphoglycerate ⇌ 2-phosphoglycerate	4.4	0 to 0.8
⑨ 2-Phosphoglycerate ⇌ phosphoenolpyruvate + H_2O	7.5	0 to 3.3
⑩ Phosphoenolpyruvate + ADP ⟶ pyruvate + ATP	−31.4	−16.7

Note: $\Delta G'^{\circ}$ is the standard free-energy change, as defined in Chapter 13 (p. 491). ΔG is the free-energy change calculated from the actual concentrations of glycolytic intermediates present under physiological conditions in erythrocytes, at pH 7. The glycolytic reactions bypassed in gluconeogenesis are shown in red. Biochemical equations are not necessarily balanced for H or charge (p. 506).

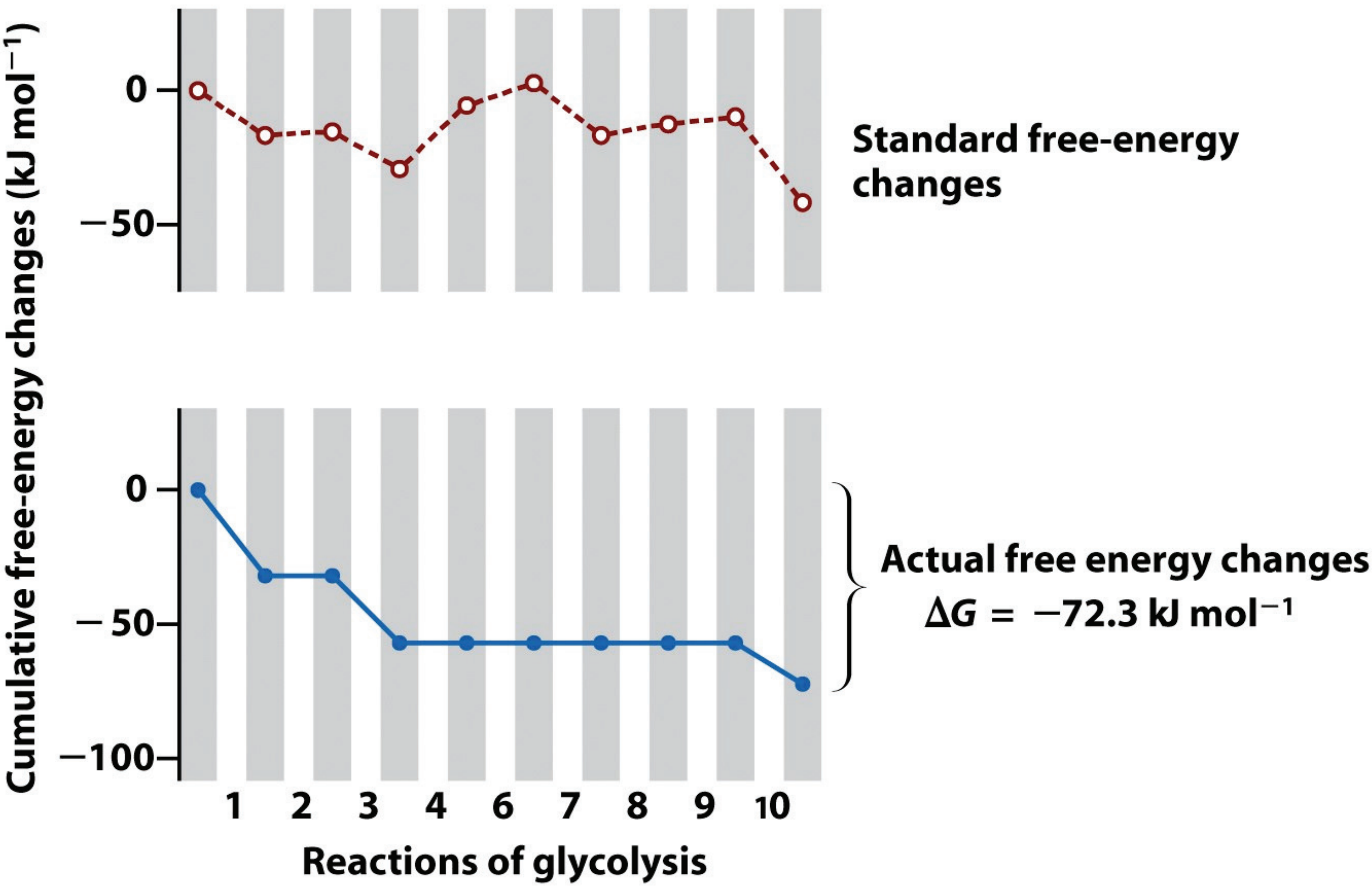
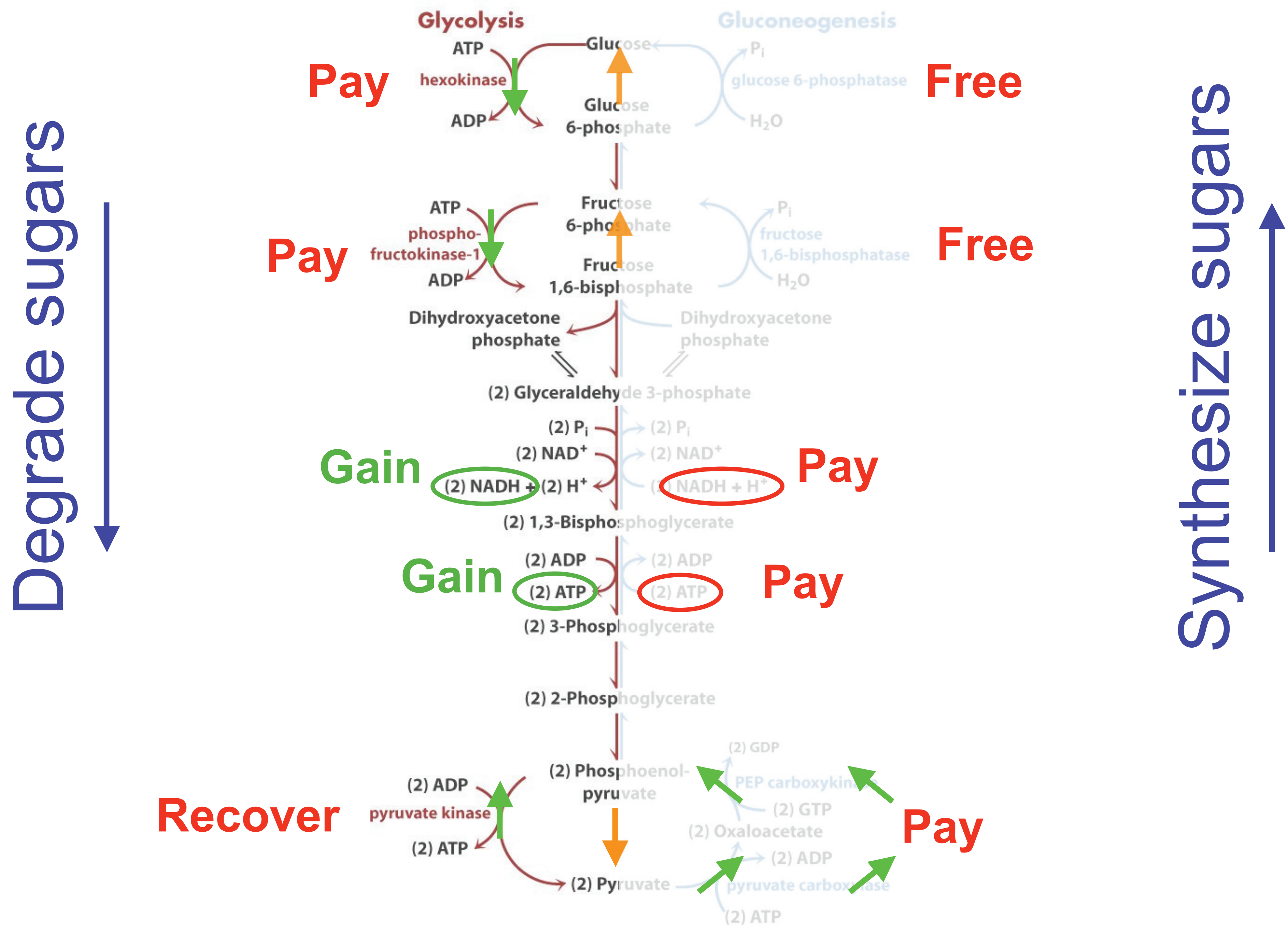
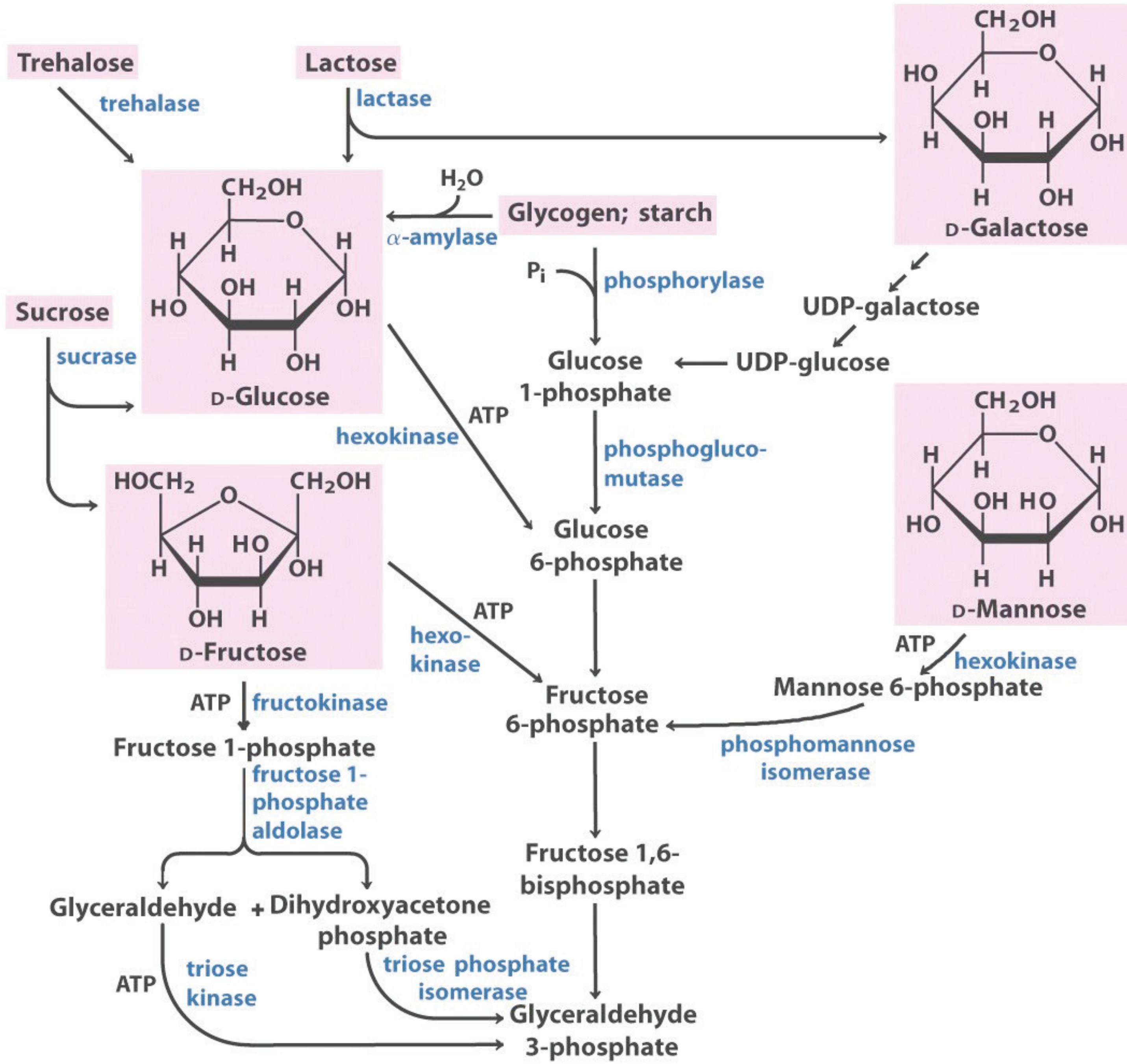
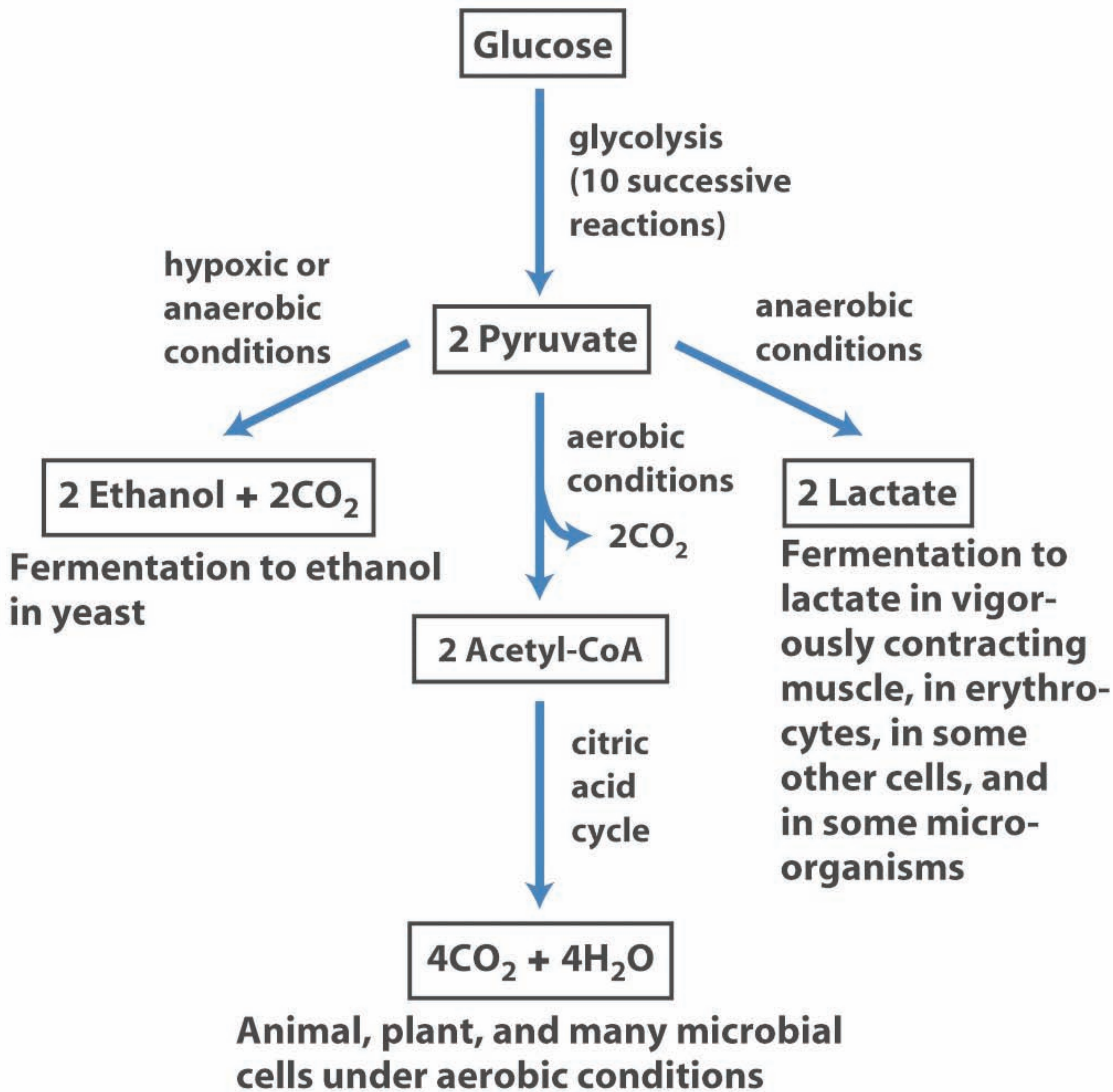


Figure 11-11 Principles of Biochemistry, 4/e

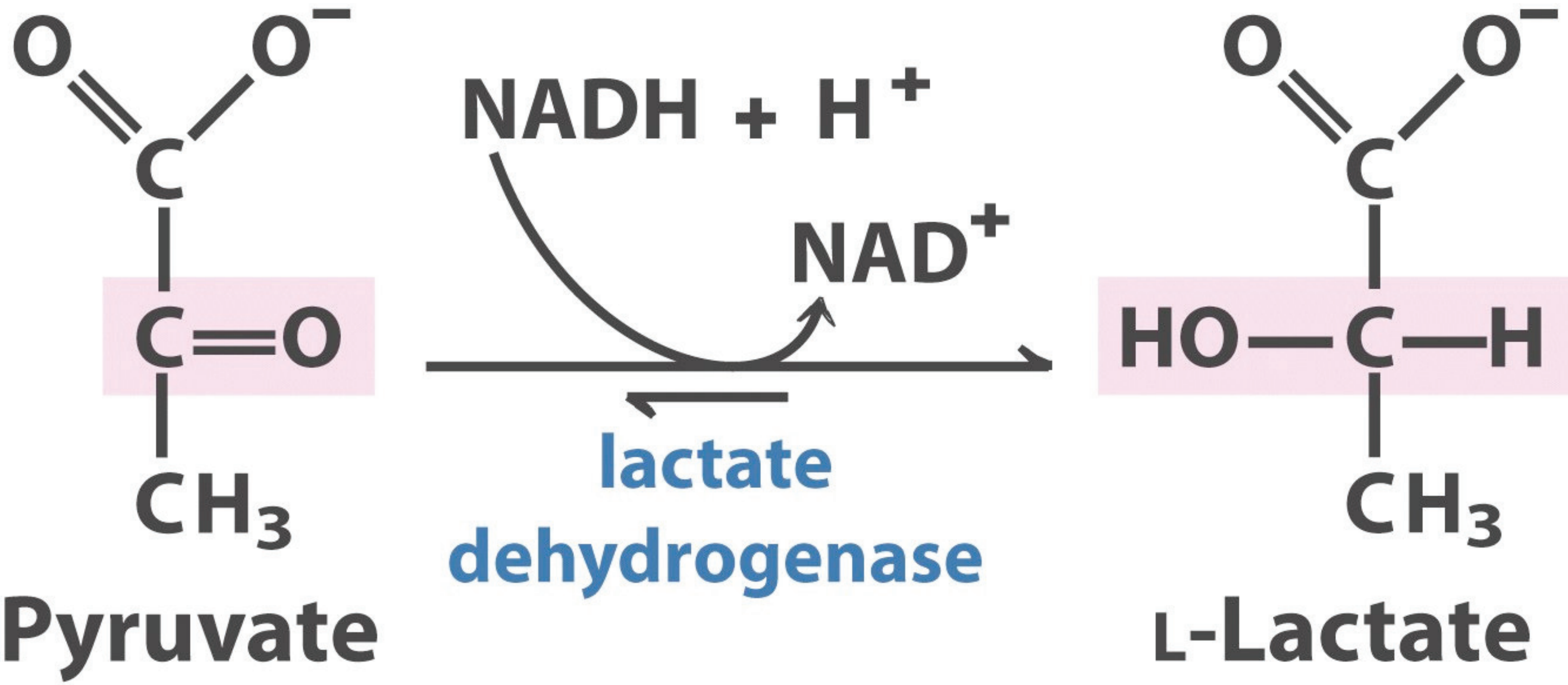

Degrade sugars
Synthesize sugars
Glycolysis
Gluconeogenesis
Pay
Free
Pay
Free
Gain
Pay
Gain
Pay
Recover
Pay
ATP
hexokinase
ADP
Glucose
Glucose 6-phosphate
P_i
glucose 6-phosphatase
H_2O
ATP
phospho-fructokinase-1
ADP
Fructose 6-phosphate
Fructose 1,6-bisphosphate
P_i
fructose 1,6-bisphosphatase
H_2O
Dihydroxyacetone phosphate
Dihydroxyacetone phosphate
(2) Glyceraldehyde 3-phosphate
(2) P_i
(2) NAD^+
(2) NADH + (2) H^+
(2) P_i
(2) NAD^+
(2) NADH + H^+
(2) 1,3-Bisphosphoglycerate
(2) ADP
(2) ATP
(2) ADP
(2) ATP
(2) 3-Phosphoglycerate
(2) 2-Phosphoglycerate
(2) Phosphoenol-pyruvate
(2) ADP
pyruvate kinase
(2) ATP
(2) GDP
PEP carboxykinase
(2) GTP
(2) Oxaloacetate
(2) ADP
(2) Pyruvate
pyruvate carboxylase
(2) ATP


Trehalose
trehalase
Lactose
lactase
Sucrose
sucrase
D-Glucose
H2O
α-amylase
Glycogen; starch
Pi
phosphorylase
D-Galactose
UDP-galactose
UDP-glucose
Glucose 1-phosphate
phosphogluco-mutase
ATP
hexokinase
Glucose 6-phosphate
D-Fructose
D-Mannose
ATP
hexo-kinase
ATP
hexokinase
Mannose 6-phosphate
Fructose 6-phosphate
phosphomannose isomerase
ATP
fructokinase
Fructose 1-phosphate
fructose 1-phosphate aldolase
Glyceraldehyde + Dihydroxyacetone phosphate
Fructose 1,6-bisphosphate
ATP
triose kinase
triose phosphate isomerase
Glyceraldehyde 3-phosphate

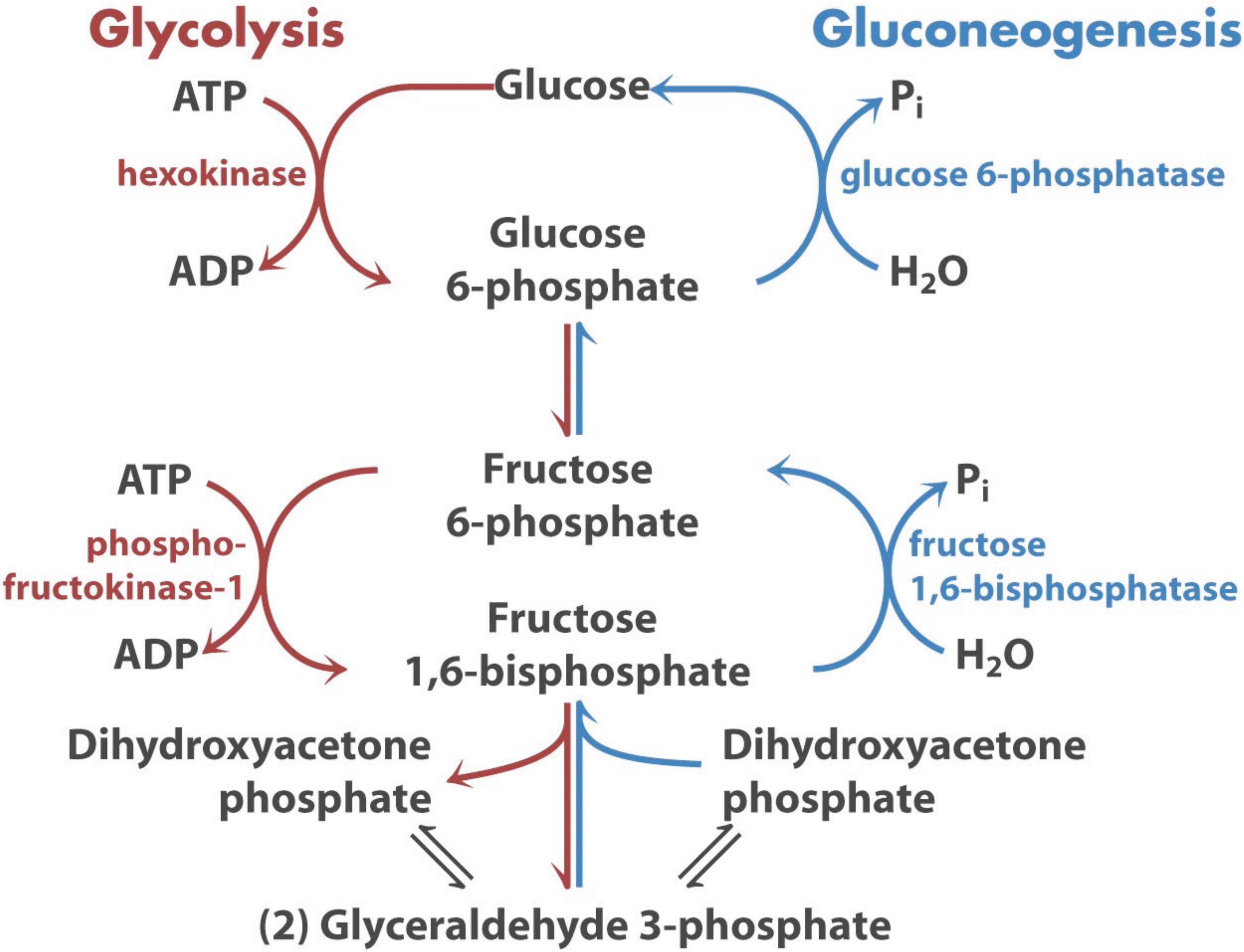

Glucose
glycolysis
(10 successive
reactions)
hypoxic or
anaerobic
conditions
2 Pyruvate
anaerobic
conditions
aerobic
conditions
2 Ethanol + $2CO_2$
$2CO_2$
2 Lactate
Fermentation to ethanol
in yeast
Fermentation to
lactate in vigor-
ously contracting
muscle, in erythro-
cytes, in some
other cells, and
in some micro-
organisms
2 Acetyl-CoA
citric
acid
cycle
$4CO_2 + 4H_2O$
Animal, plant, and many microbial
cells under aerobic conditions

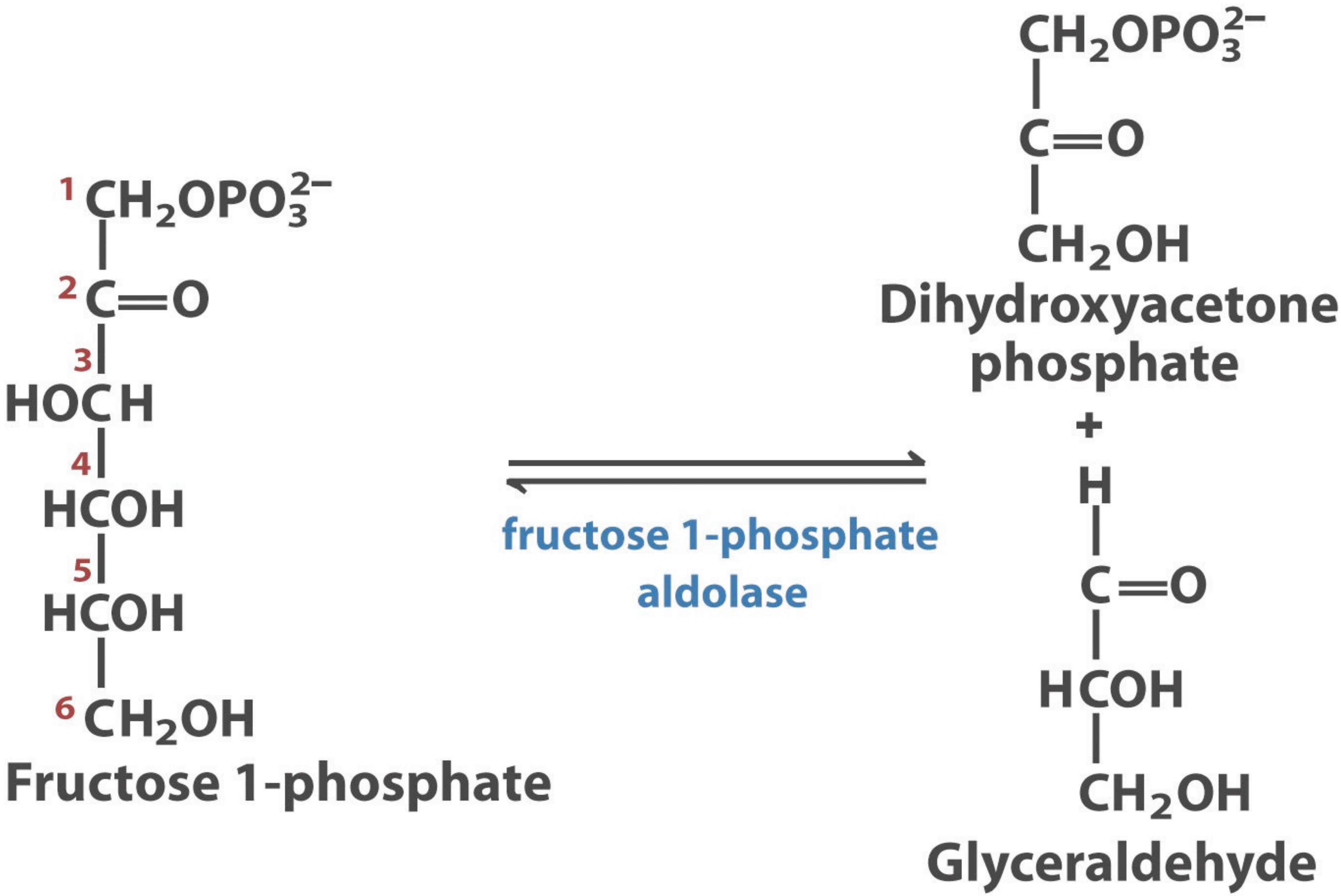
Pyruvate (enol form)

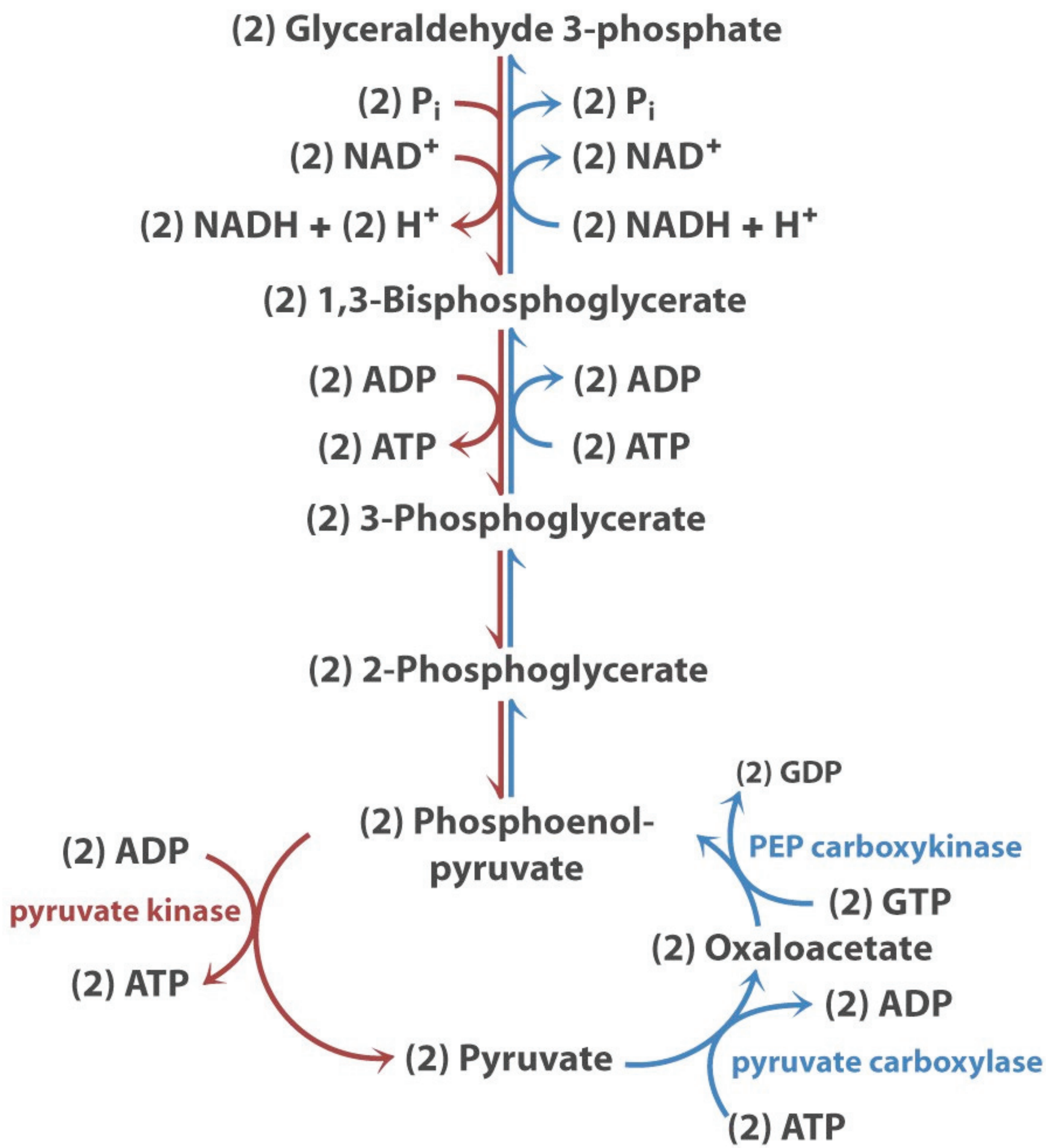
Pyruvate (keto form)



$\Delta G'^{\circ} = -\ 25.1$ kJ/mol


Glycolysis
Gluconeogenesis
Glucose
ATP
hexokinase
ADP
P_i
glucose 6-phosphatase
H_2O
Glucose
6-phosphate
Fructose
6-phosphate
ATP
phospho-
fructokinase-1
ADP
P_i
fructose
1,6-bisphosphatase
H_2O
Fructose
1,6-bisphosphate
Dihydroxyacetone
phosphate
Dihydroxyacetone
phosphate
(2) Glyceraldehyde 3-phosphate


1 CH2OPO3 2−
2 C=O
3 HOCH
4 HCOH
5 HCOH
6 CH2OH
Fructose 1-phosphate
fructose 1-phosphate
aldolase
CH2OPO3 2−
C=O
CH2OH
Dihydroxyacetone
phosphate
+
H
C=O
HCOH
CH2OH
Glyceraldehyde



(2) Glyceraldehyde 3-phosphate
(2) P_i
(2) NAD^+
(2) NADH + (2) H^+
(2) P_i
(2) NAD^+
(2) NADH + H^+
(2) 1,3-Bisphosphoglycerate
(2) ADP
(2) ATP
(2) ADP
(2) ATP
(2) 3-Phosphoglycerate
(2) 2-Phosphoglycerate
(2) Phosphoenol-
pyruvate
(2) ADP
pyruvate kinase
(2) ATP
(2) Pyruvate
(2) GDP
PEP carboxykinase
(2) GTP
(2) Oxaloacetate
(2) ADP
pyruvate carboxylase
(2) ATP