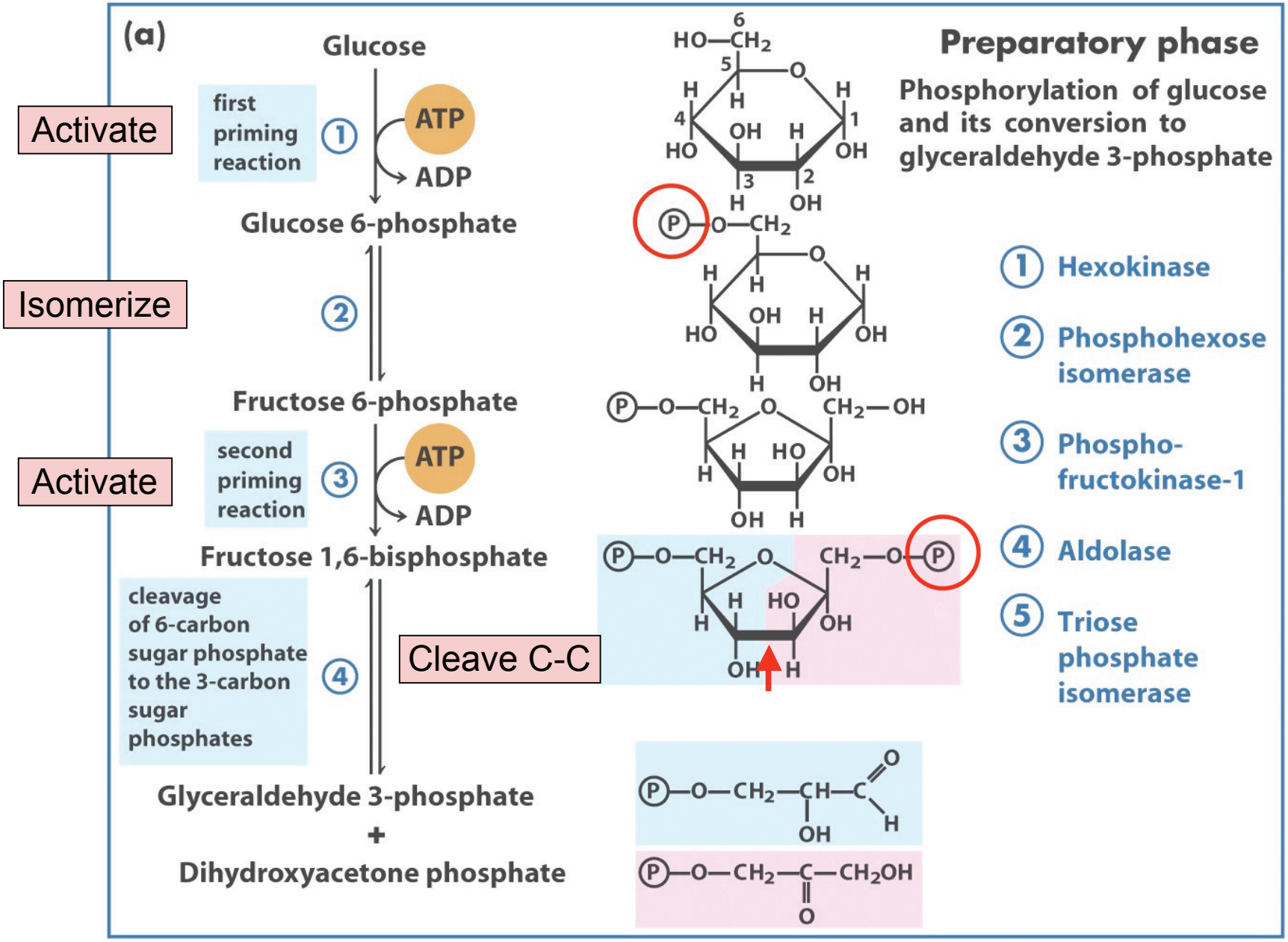
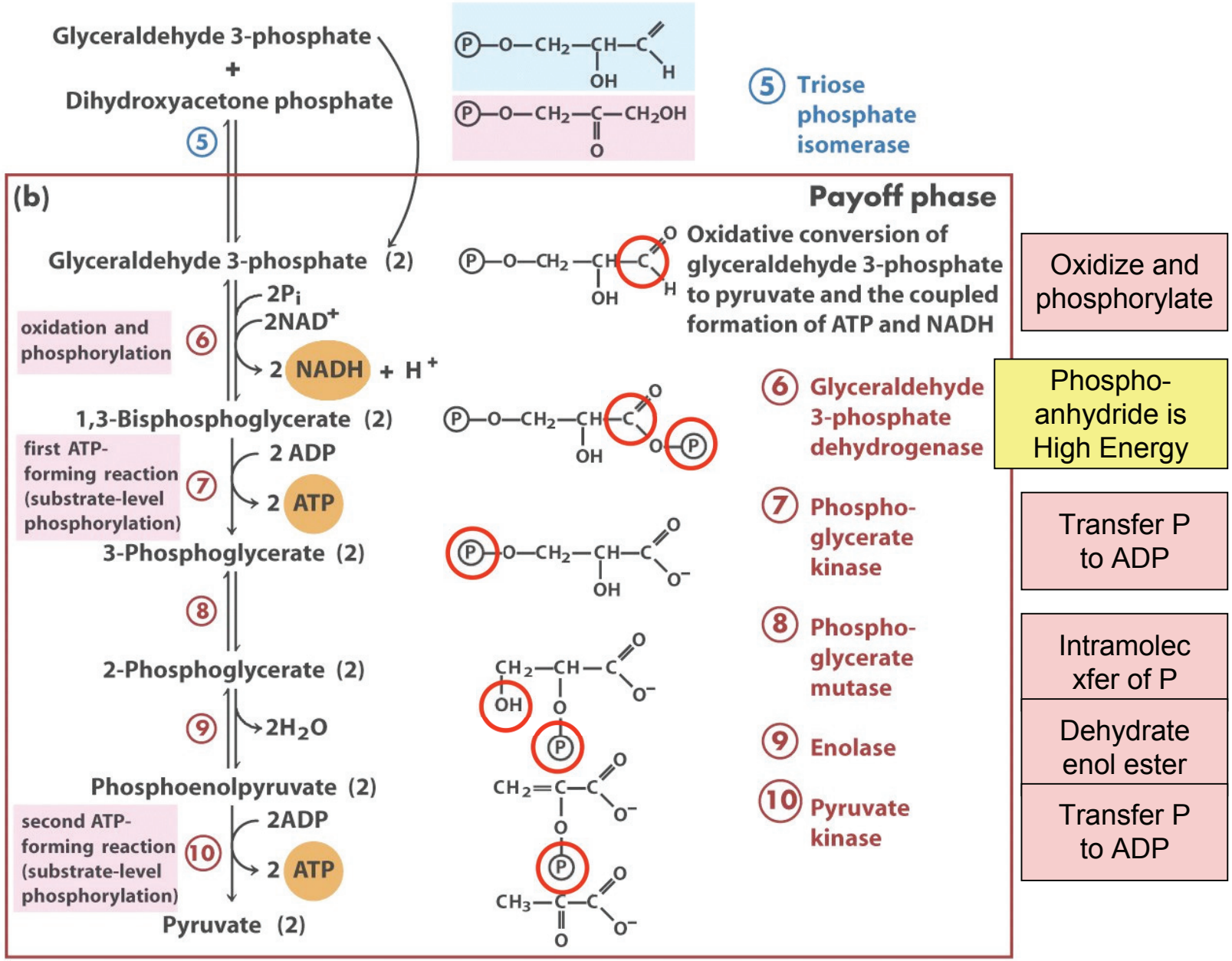
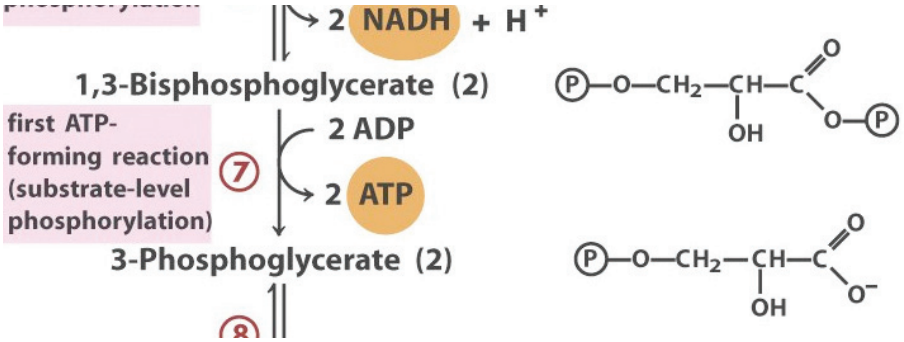

(a)
Glucose
first priming reaction
1
ATP
ADP
Glucose 6-phosphate
2
Fructose 6-phosphate
second priming reaction
3
ATP
ADP
Fructose 1,6-bisphosphate
cleavage of 6-carbon sugar phosphate to the 3-carbon sugar phosphates
4
Glyceraldehyde 3-phosphate
+
Dihydroxyacetone phosphate
Activate
Isomerize
Activate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


Glyceraldehyde 3-phosphate
+
Dihydroxyacetone phosphate
5
5 Triose phosphate isomerase
(b)
Payoff phase
Glyceraldehyde 3-phosphate (2)
Oxidative conversion of glyceraldehyde 3-phosphate to pyruvate and the coupled formation of ATP and NADH
oxidation and phosphorylation
6
2Pi
2NAD+
2 NADH + H+
1,3-Bisphosphoglycerate (2)
6 Glyceraldehyde 3-phosphate dehydrogenase
first ATP-forming reaction (substrate-level phosphorylation)
7
2 ADP
2 ATP
3-Phosphoglycerate (2)
7 Phospho-glycerate kinase
8
2-Phosphoglycerate (2)
8 Phospho-glycerate mutase
9
2H2O
Phosphoenolpyruvate (2)
9 Enolase
second ATP-forming reaction (substrate-level phosphorylation)
10
2ADP
2 ATP
Pyruvate (2)
10 Pyruvate kinase
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

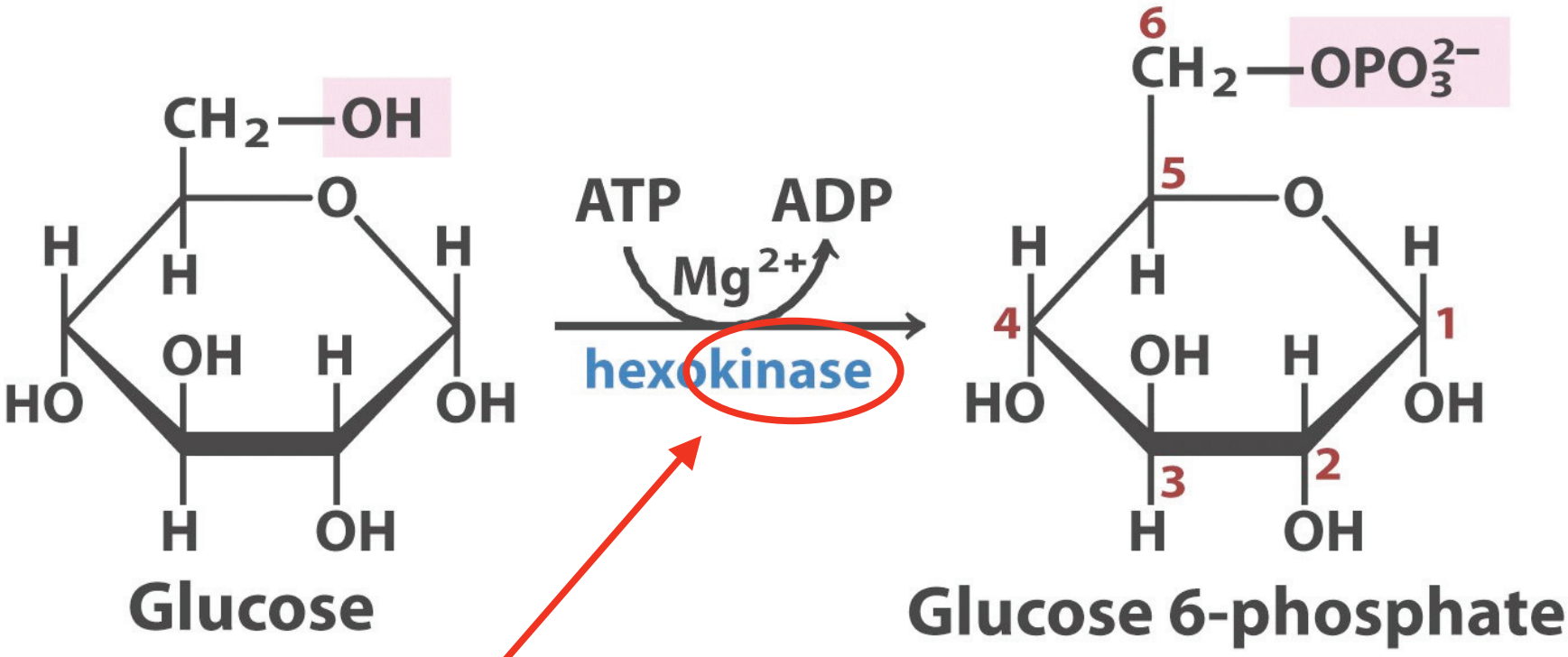
So the reaction drives hydrolysis *backwards* - makes ATP from ADP

Energy has been STORED.

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

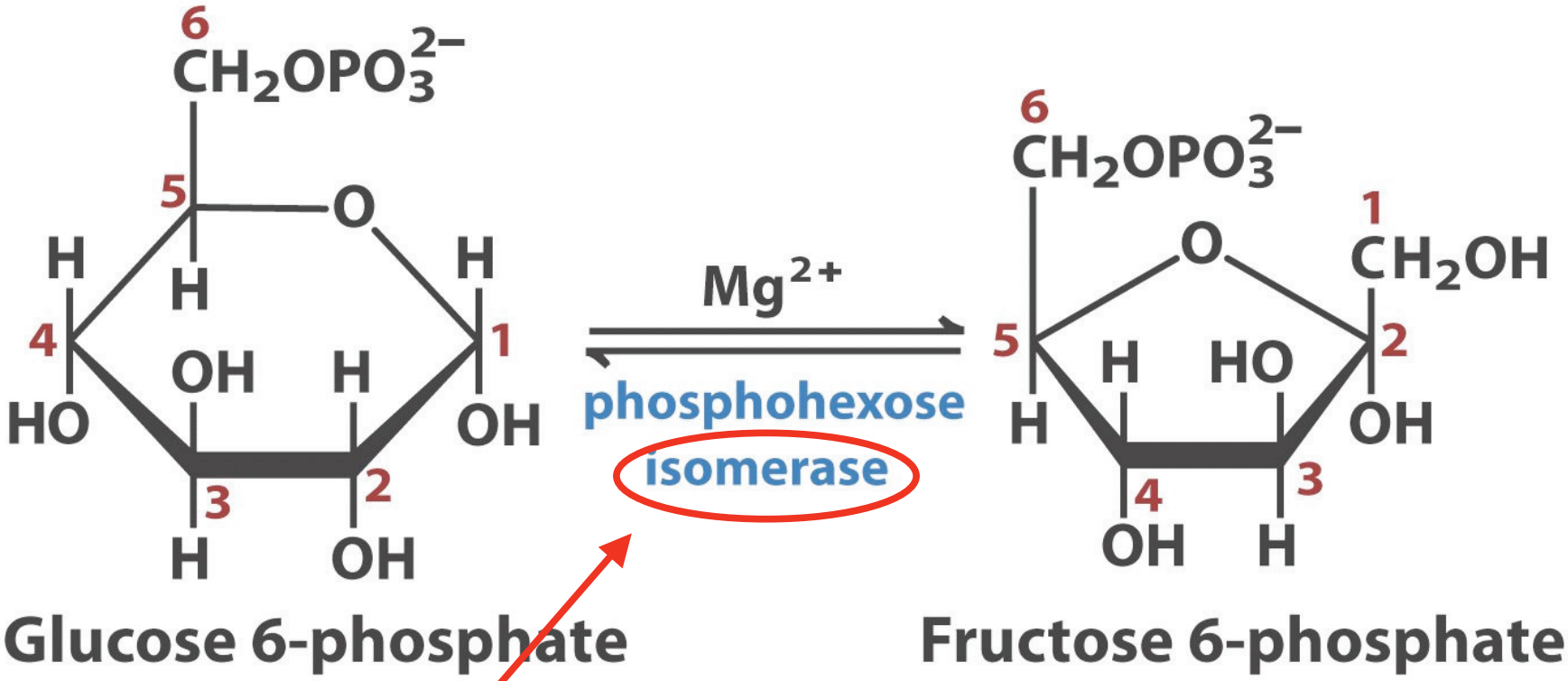
	$\Delta G'^{\circ}$ (kJ/mol)	$\Delta G'^{\circ}$ (kcal/mol)
Phosphoenolpyruvate	−61.9	−14.8
1,3-bisphosphoglycerate ($\rightarrow$ 3-phosphoglycerate + P_i)	−49.3	−11.8
Phosphocreatine	−43.0	−10.3
ADP ($\rightarrow$ AMP + P_i)	−32.8	−7.8
ATP ($\rightarrow$ ADP + P_i)	−30.5	−7.3
ATP ($\rightarrow$ AMP + PP_i)	−45.6	−10.9
AMP ($\rightarrow$ adenosine + P_i)	−14.2	−3.4
PP_i ($\rightarrow$ 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.



"Kinase" transfers a phosphate from ATP

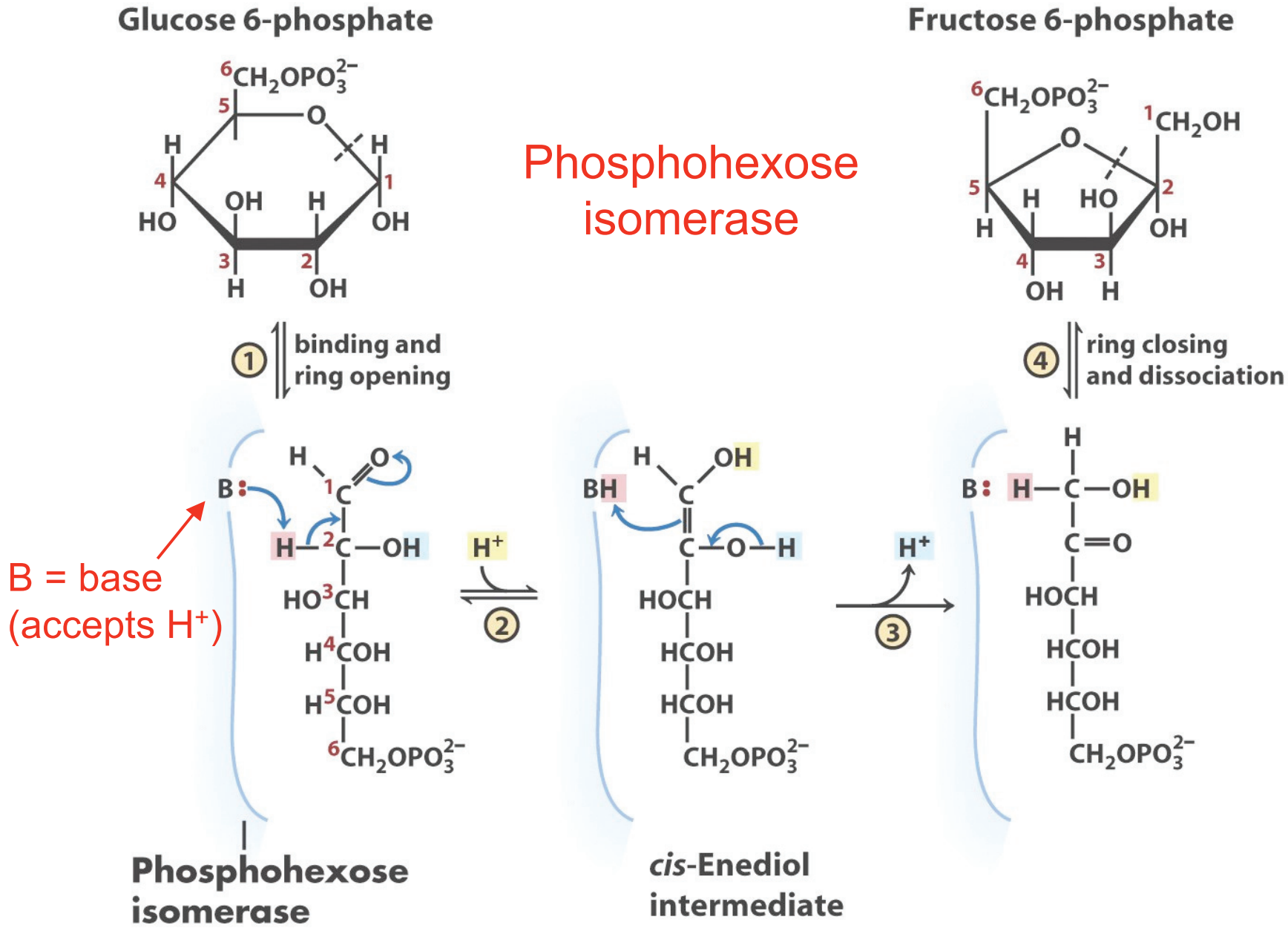
$\Delta G'^{\circ} = -16.7$ kJ/mol

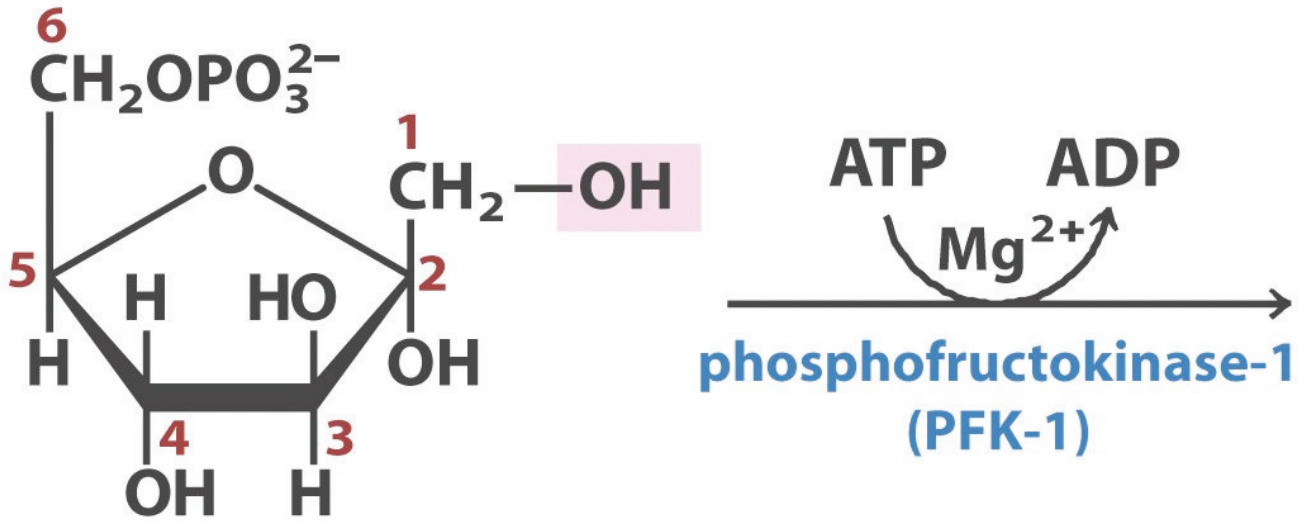


Glucose 6-phosphate **Fructose 6-phosphate**

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

"Isomerase" interconverts isomeric forms

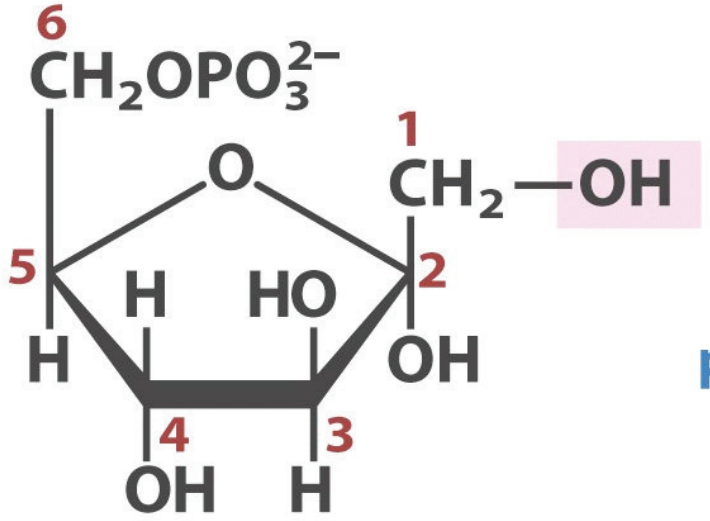

Glucose 6-phosphate
Fructose 6-phosphate
Phosphohexose isomerase
B = base (accepts H+)
1 binding and ring opening
2
3
4 ring closing and dissociation
Phosphohexose isomerase
cis-Enediol intermediate



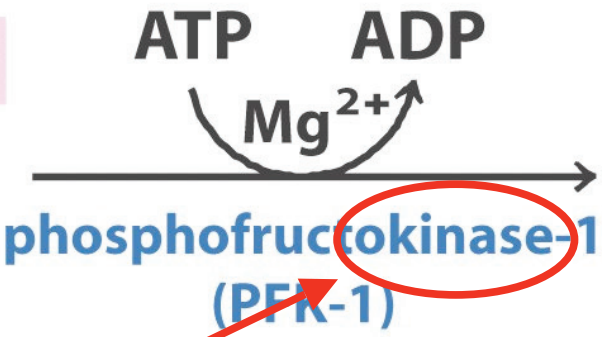
Fructose 6-phosphate

What kind of reaction do you expect this to be?

1) reduction 2) oxidation 3) isomerization 4) phosphorylation

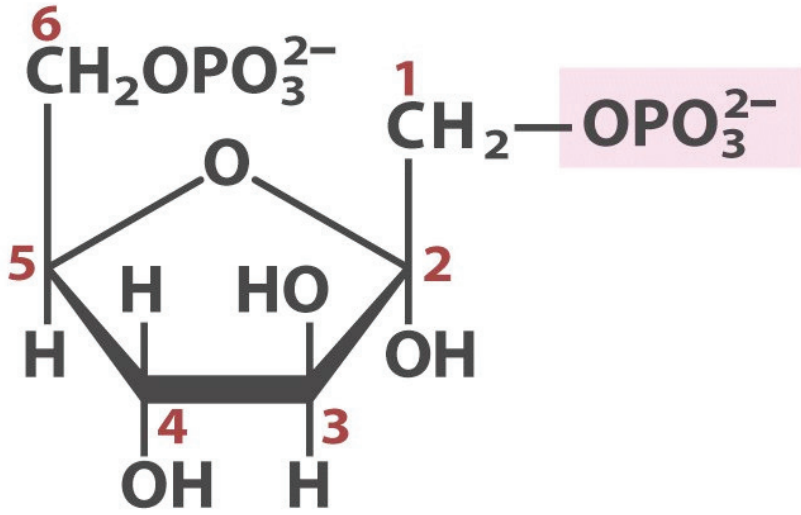


Fructose 6-phosphate



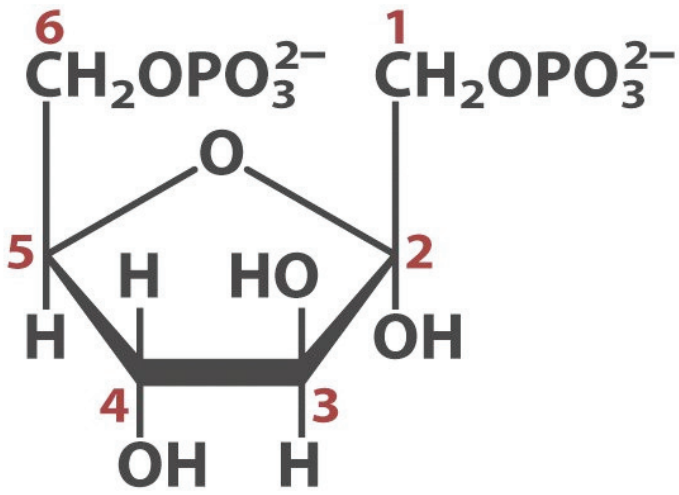
"Kinase" transfers a phosphate from ATP

4) phosphorylation

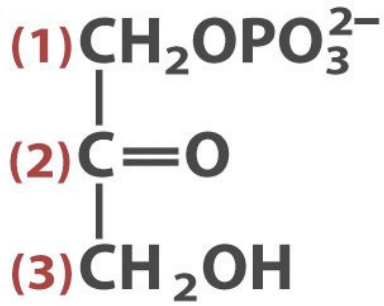


Fructose 1,6-bisphosphate

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

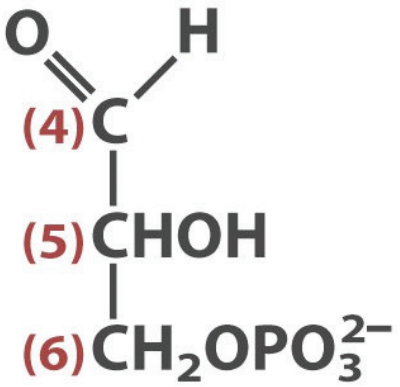


Fructose 1,6-bisphosphate



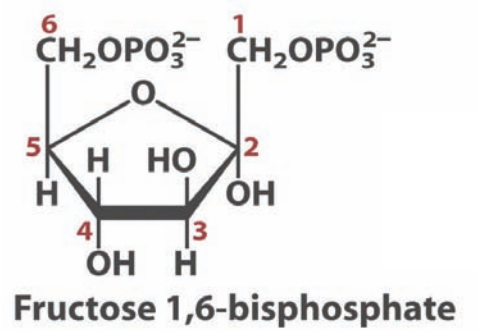
Dihydroxyacetone phosphate

+



Glyceraldehyde 3-phosphate

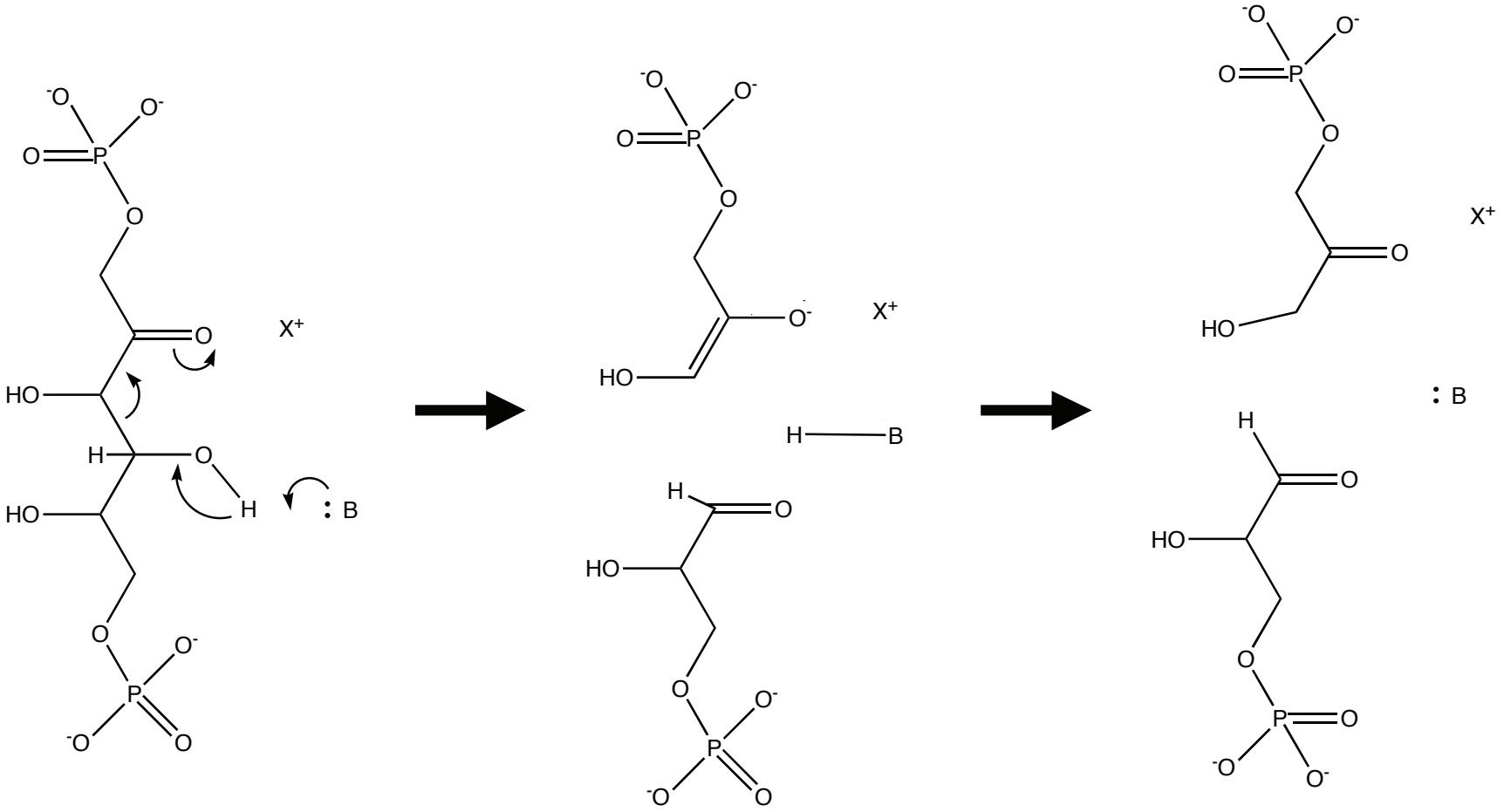
$\Delta G'^{\circ} = 23.8$ kJ/mol

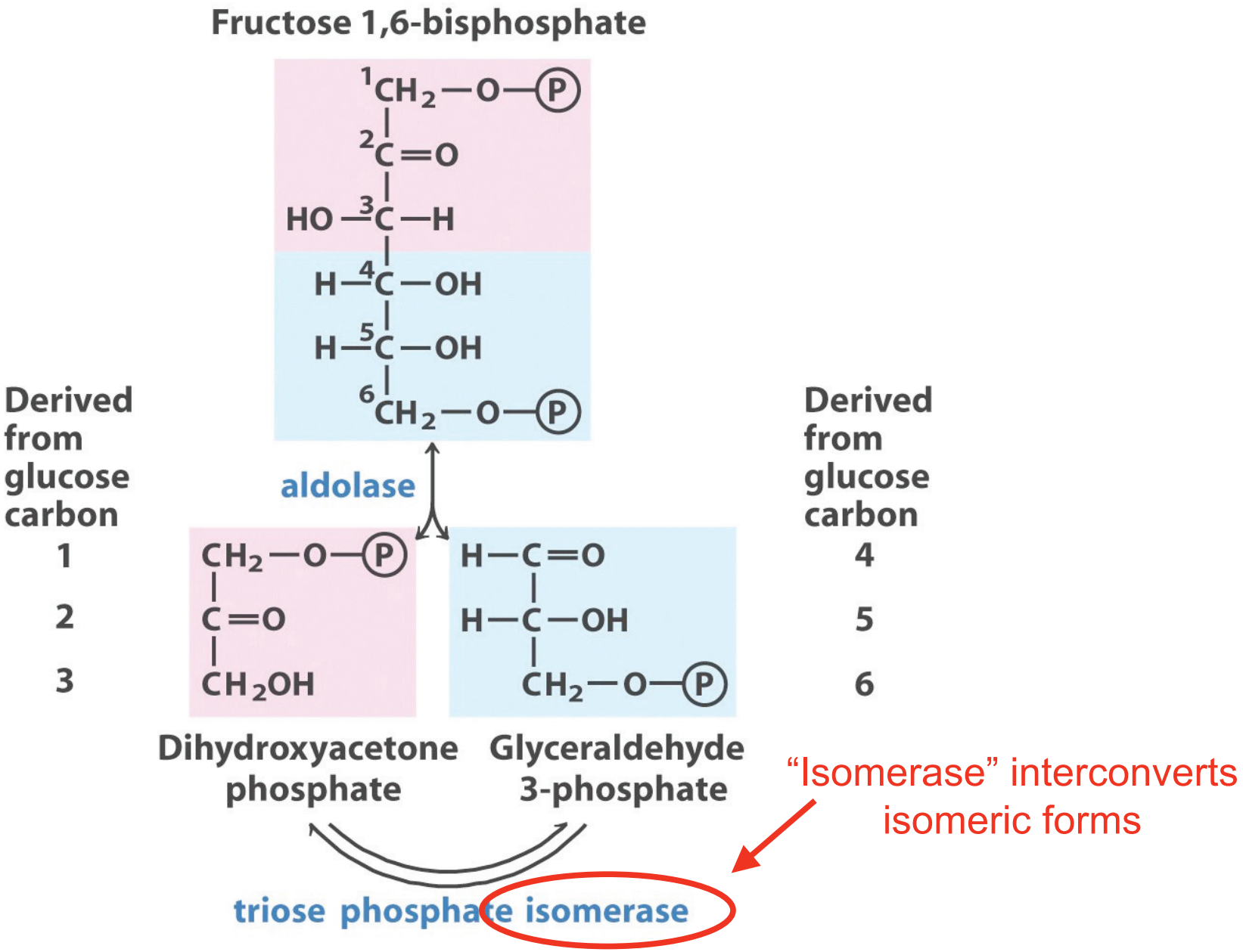


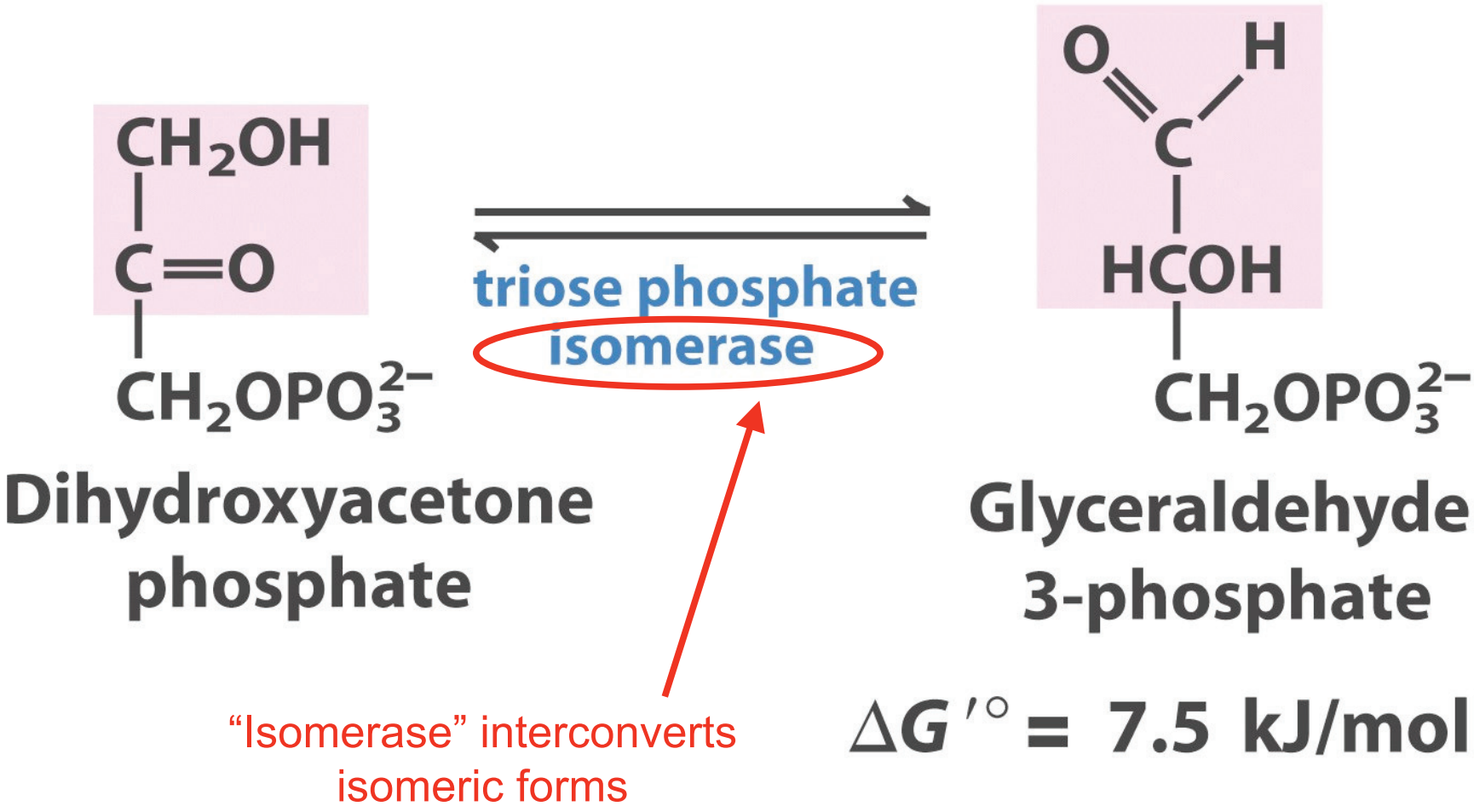
Fructose 1,6-bisphosphate

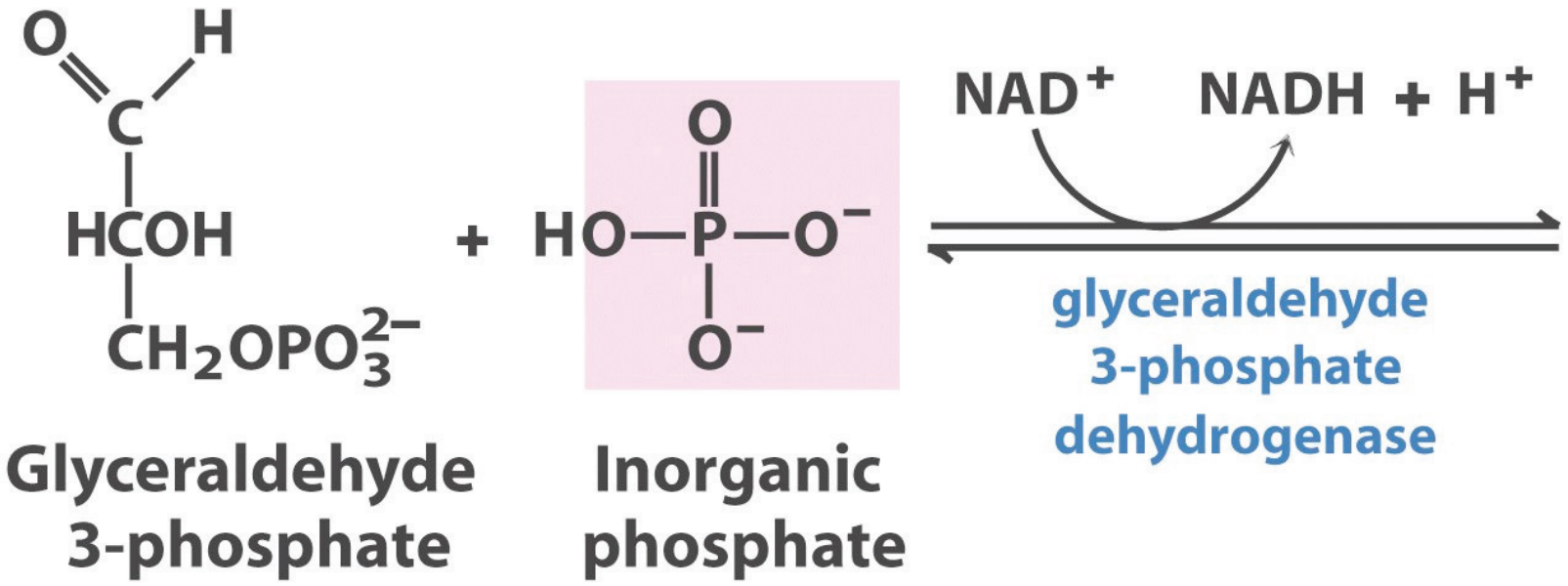
Aldolase

New reaction - same principles



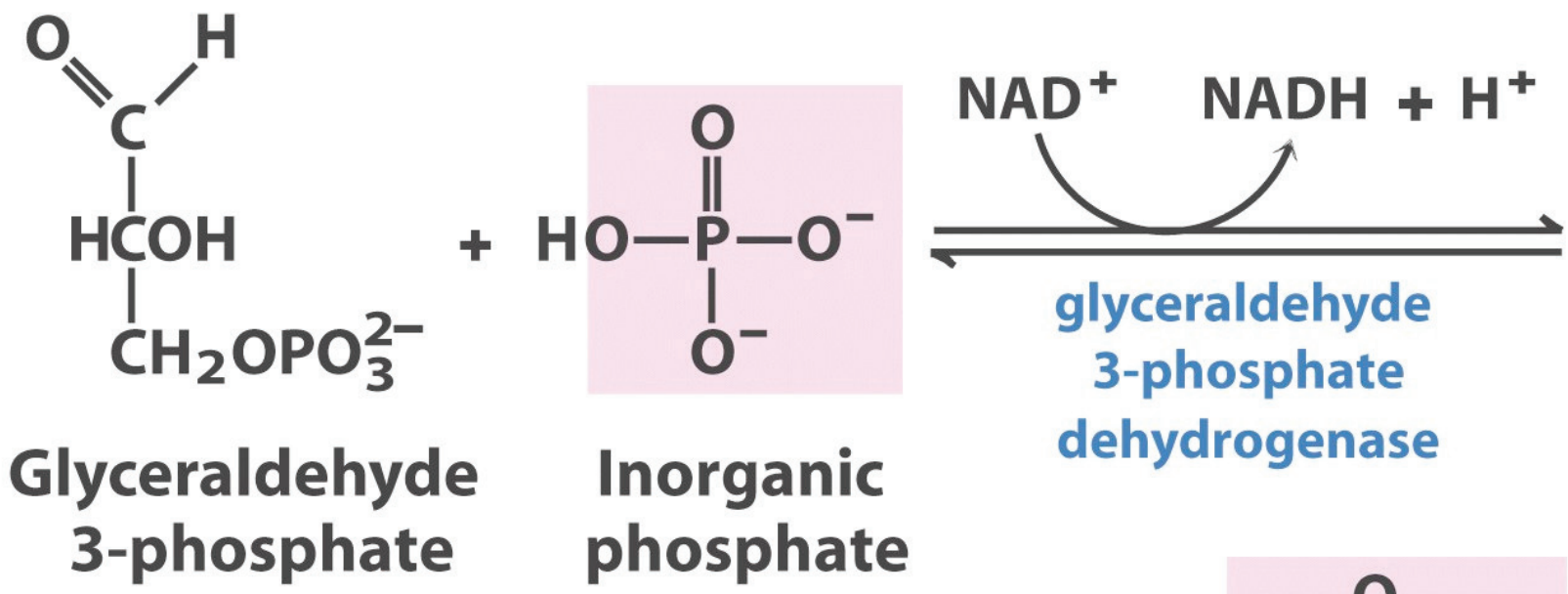

Fructose 1,6-bisphosphate
Derived from glucose carbon
1
2
3
aldolase
Derived from glucose carbon
4
5
6
Dihydroxyacetone phosphate
Glyceraldehyde 3-phosphate
triose phosphate isomerase
"Isomerase" interconverts isomeric forms


CH2OH
C=O
CH2OPO3 2–
triose phosphate
isomerase
O
H
C
HCOH
CH2OPO3 2–
Dihydroxyacetone phosphate
Glyceraldehyde 3-phosphate
ΔG′° = 7.5 kJ/mol
“Isomerase” interconverts isomeric forms



What kind of reaction do you expect this to be?

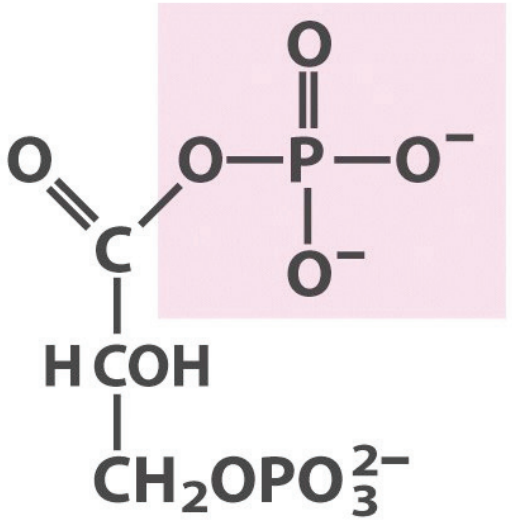
1) reduction 2) oxidation 3) isomerization 4) dehydration



What kind of reaction do you expect this to be?

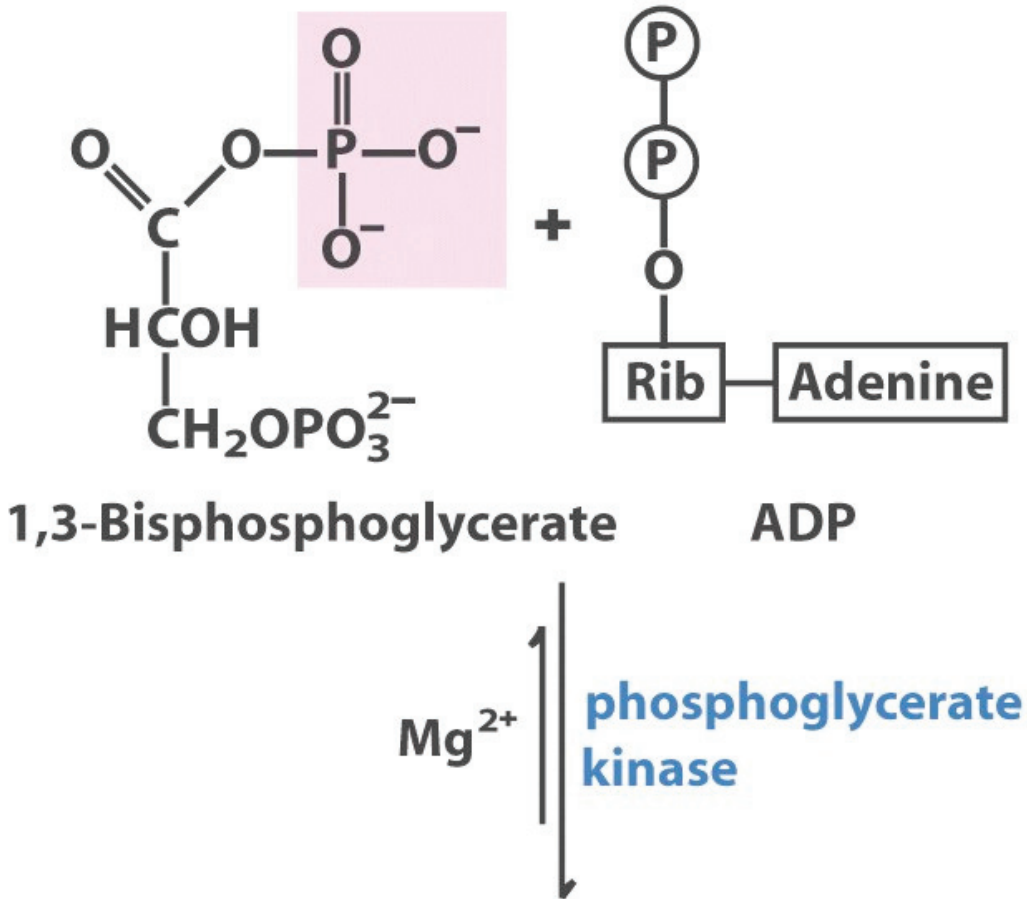
2) Oxidation

Aldehyde to a phosphorylated carboxylic acid



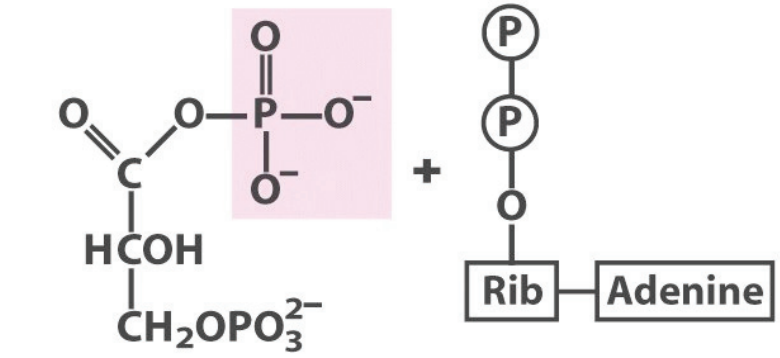
$\Delta G'^{\circ} = 6.3$ kJ/mol

1,3-Bisphosphoglycerate

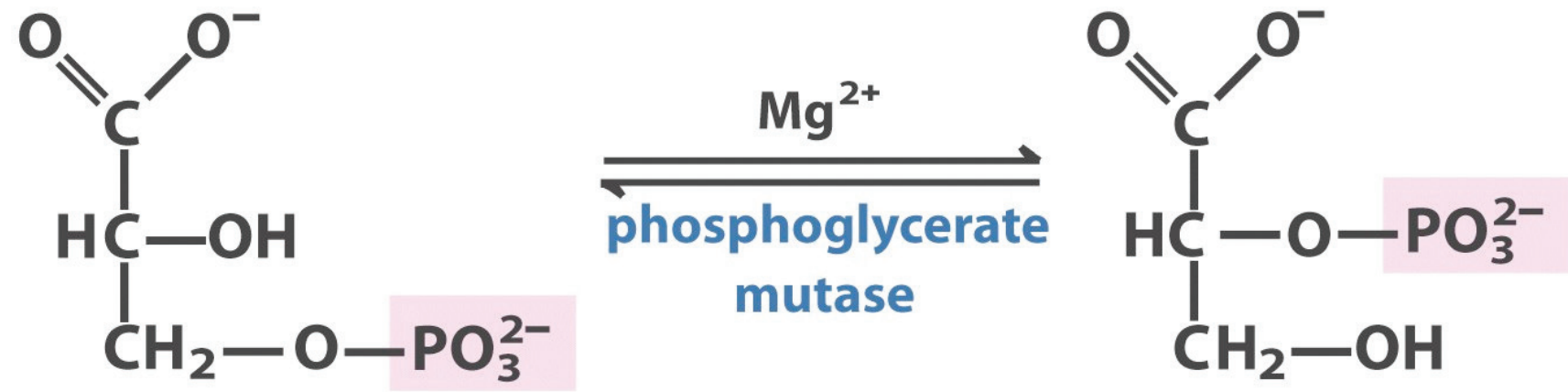


What kind of reaction do you expect this to be?

1) reduction 2) oxidation 3) phosphorylation 4) other



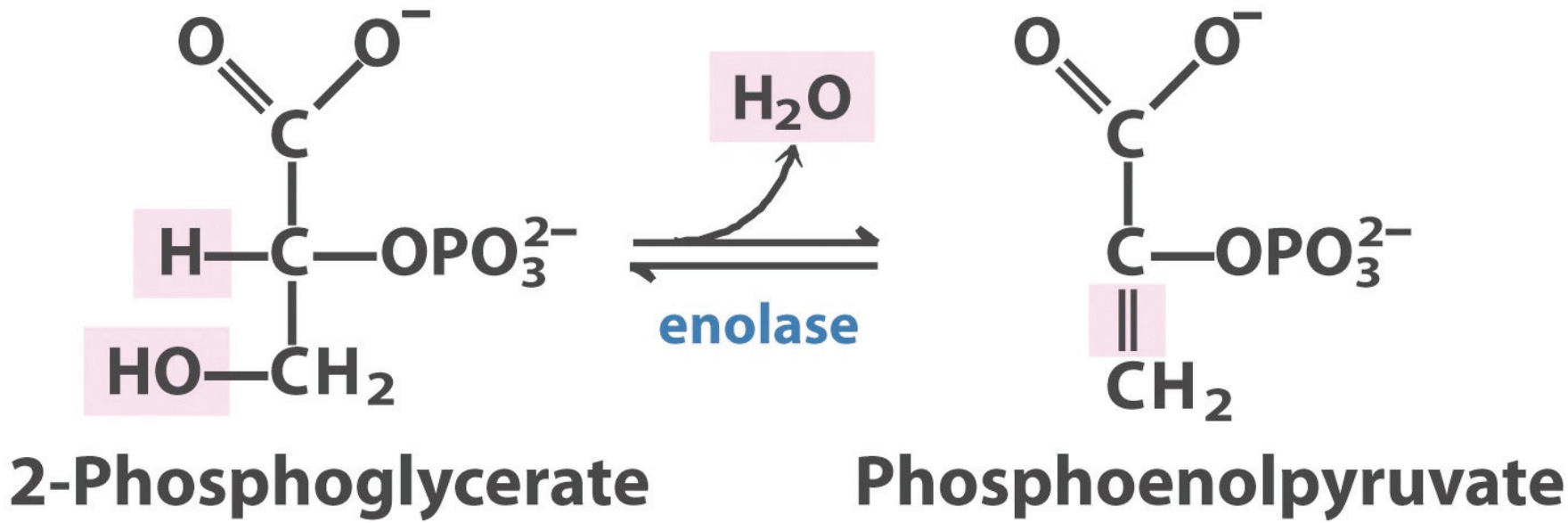
"Kinase" transfers a phosphate ***to*** ADP



3-Phosphoglycerate

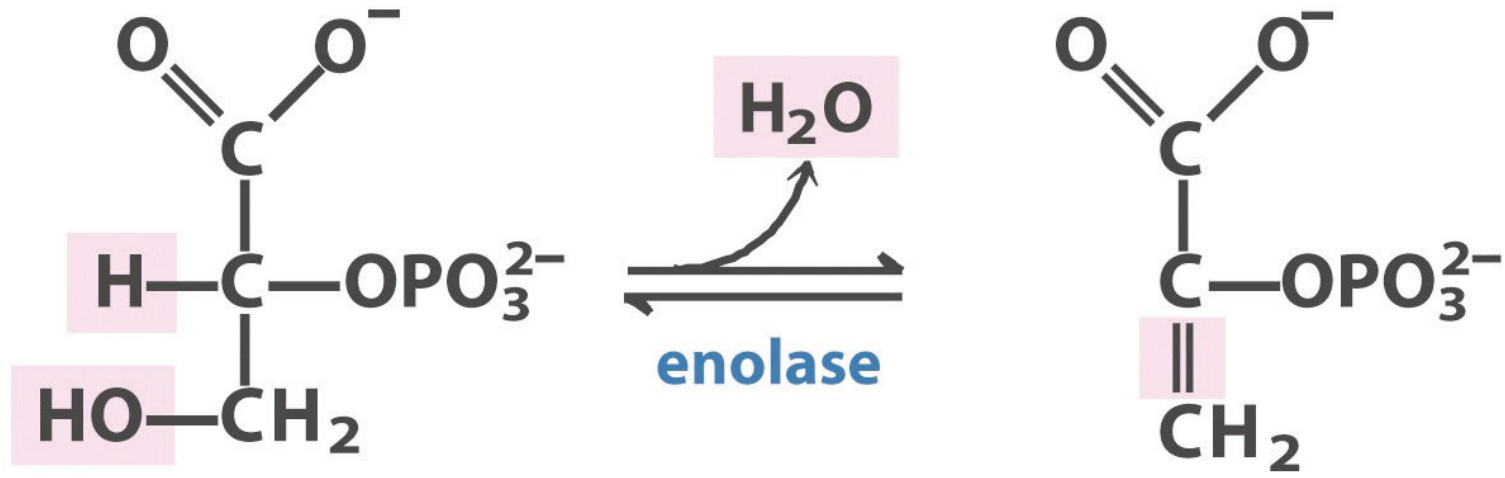
2-Phosphoglycerate

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



What kind of reaction is this?

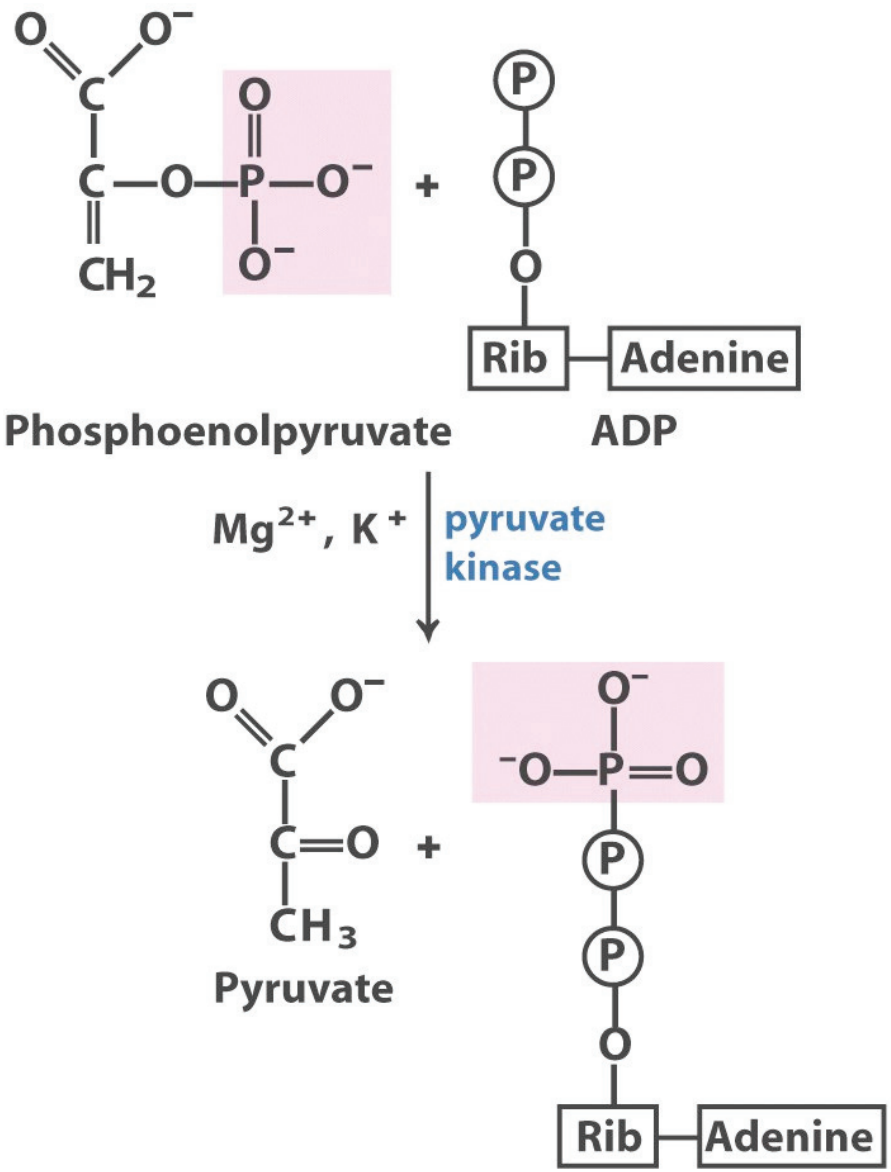
1) reduction 2) oxidation 3) isomerization 4) dehydration

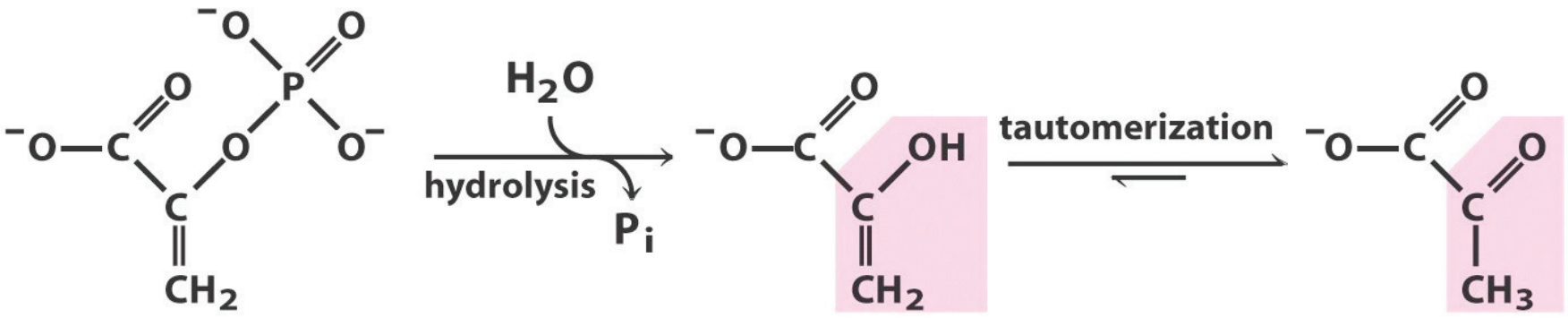


$\Delta G'^{\circ} = 7.5$ kJ/mol

What kind of reaction is this?

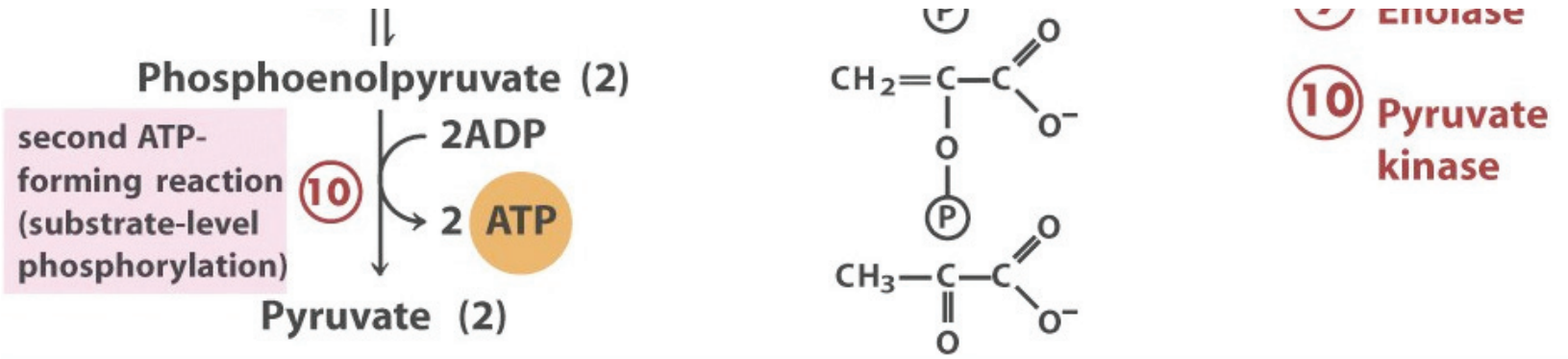
1) reduction 2) oxidation 3) isomerization 4) **dehydration**


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

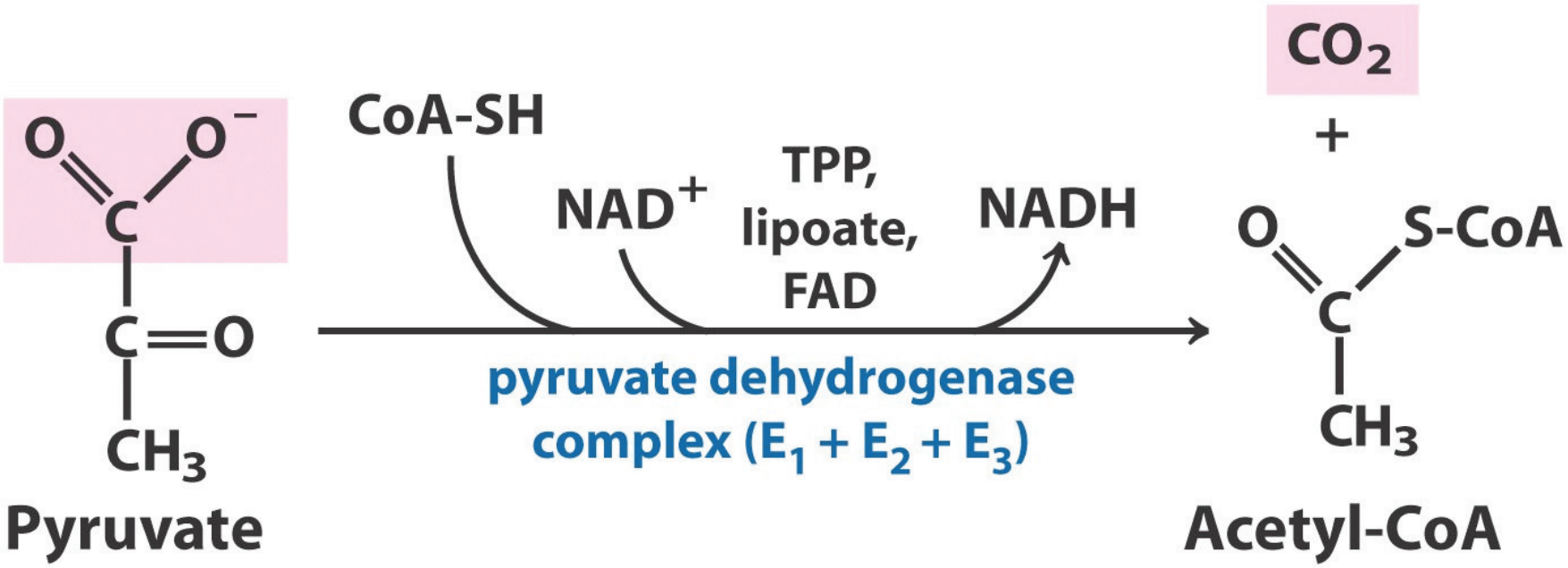


$$PEP^{3-} + H_2O \longrightarrow pyruvate^{-} + P_i^{2-}$$

$$\Delta G'^{\circ} = -61.9\ kJ/mol$$

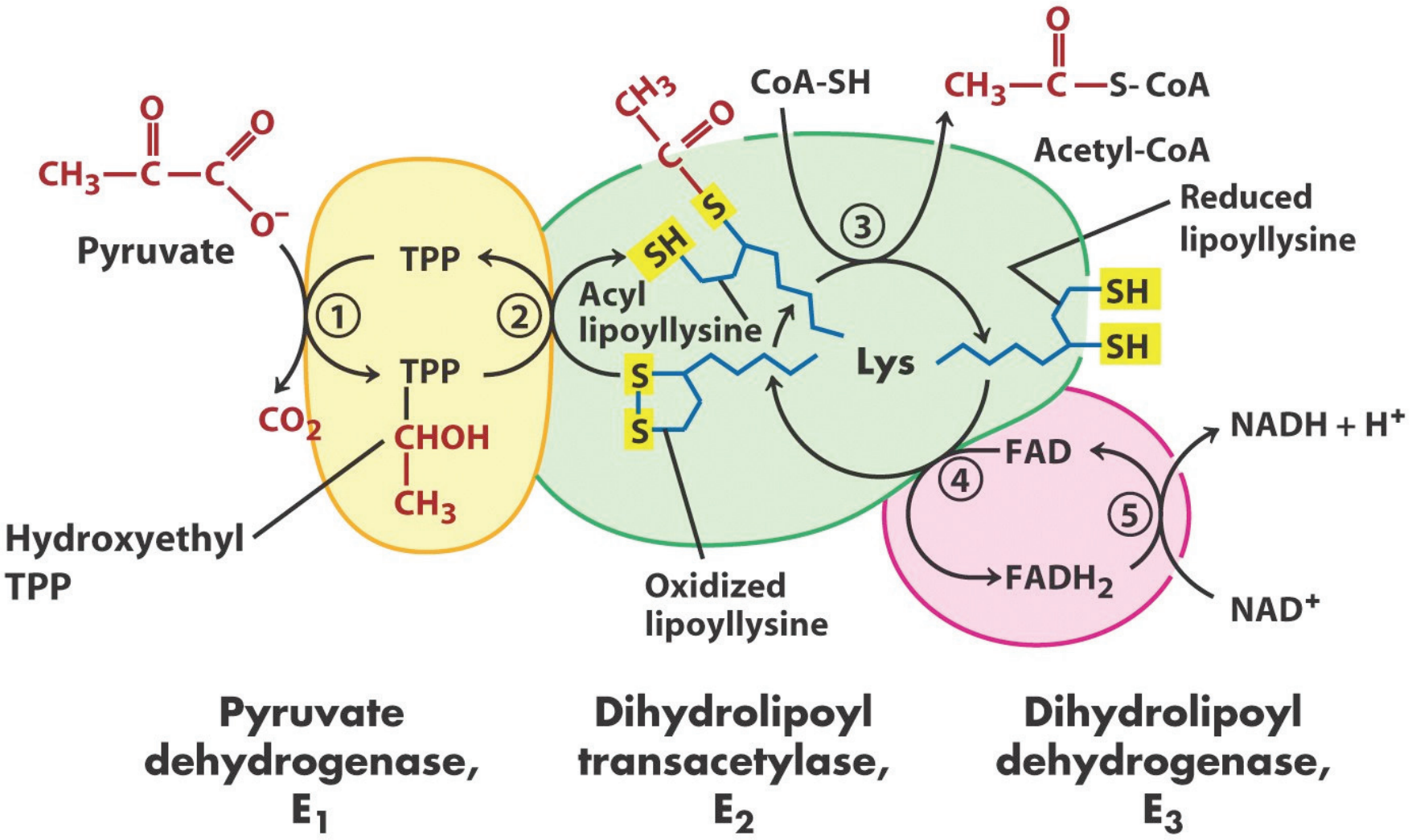


Pyruvate (3C) to Acetyl-CoA (2C) and CO_2

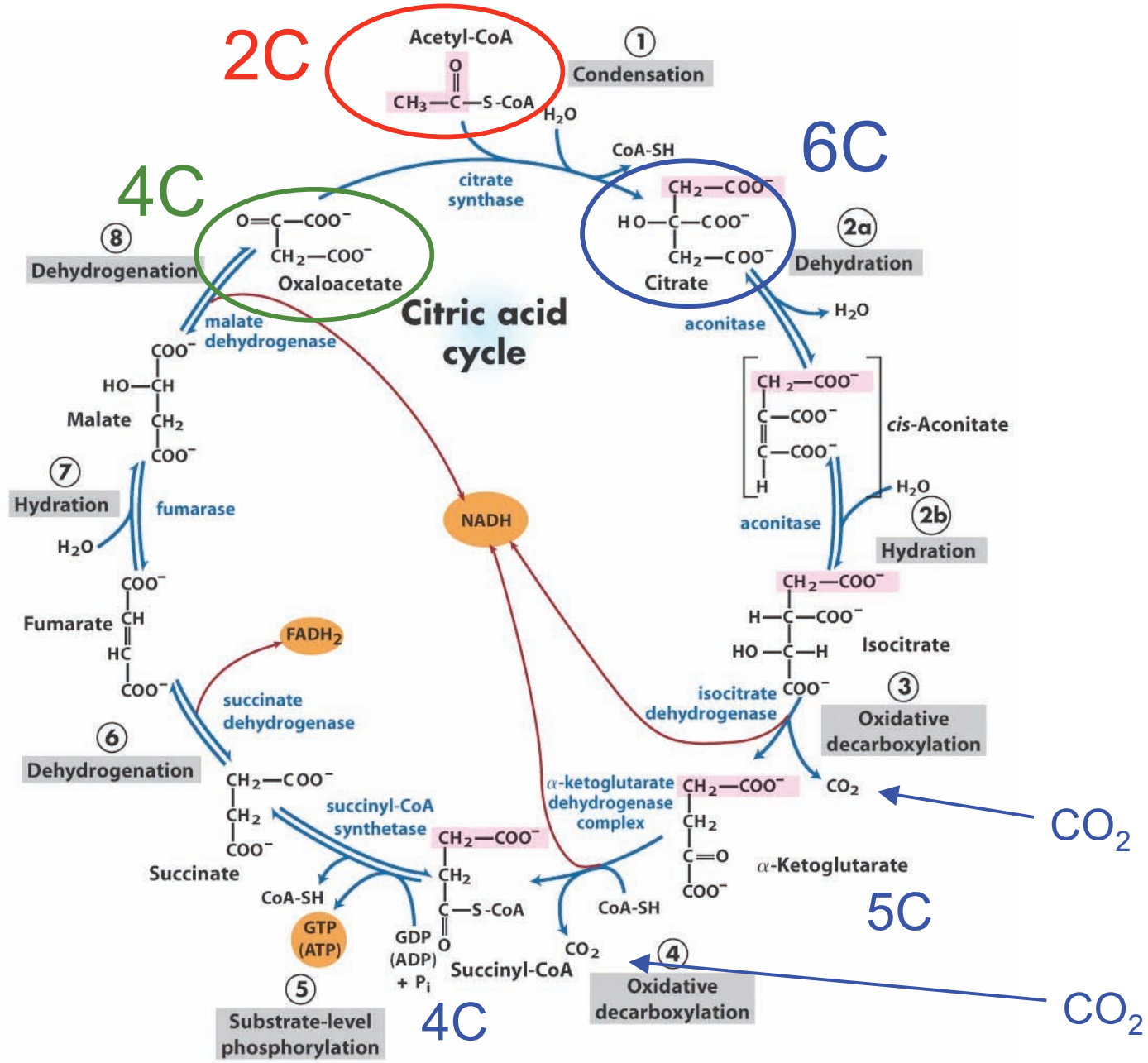


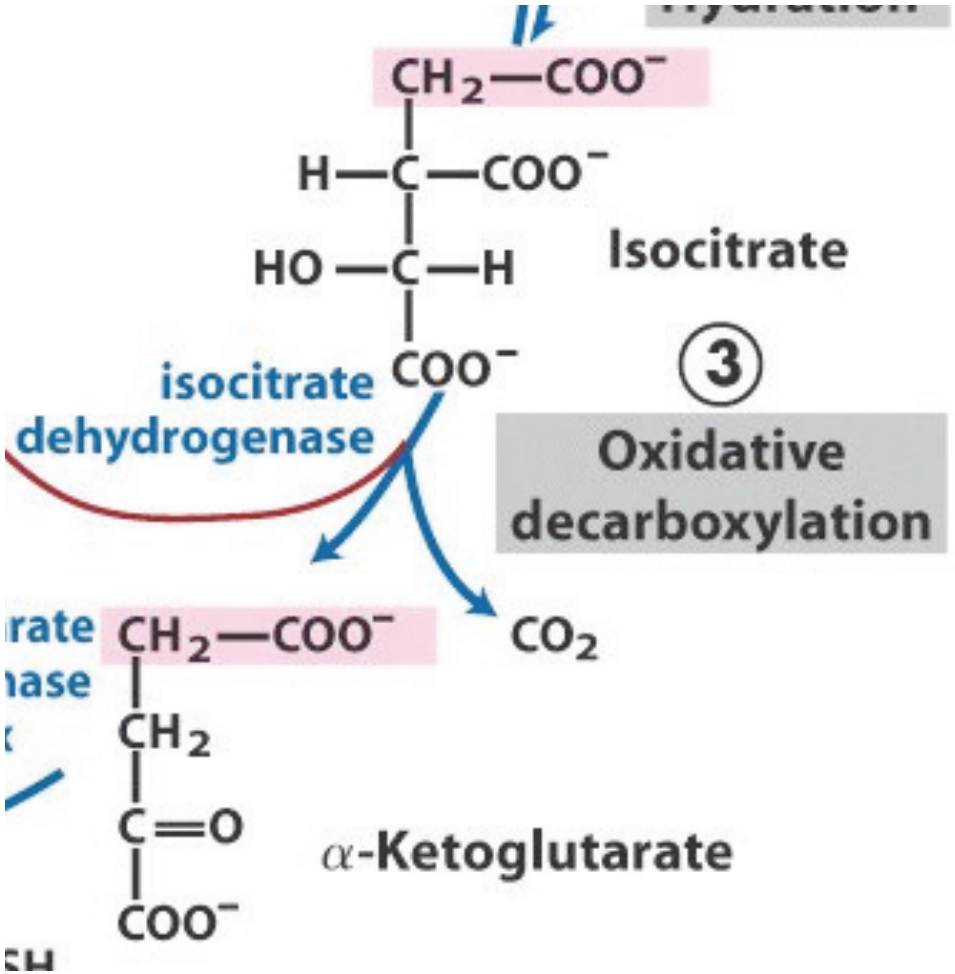
$\Delta G'^{\circ} = -33.4$ kJ/mol

Pyruvate (3C) to Acetyl-CoA (2C) and CO_2

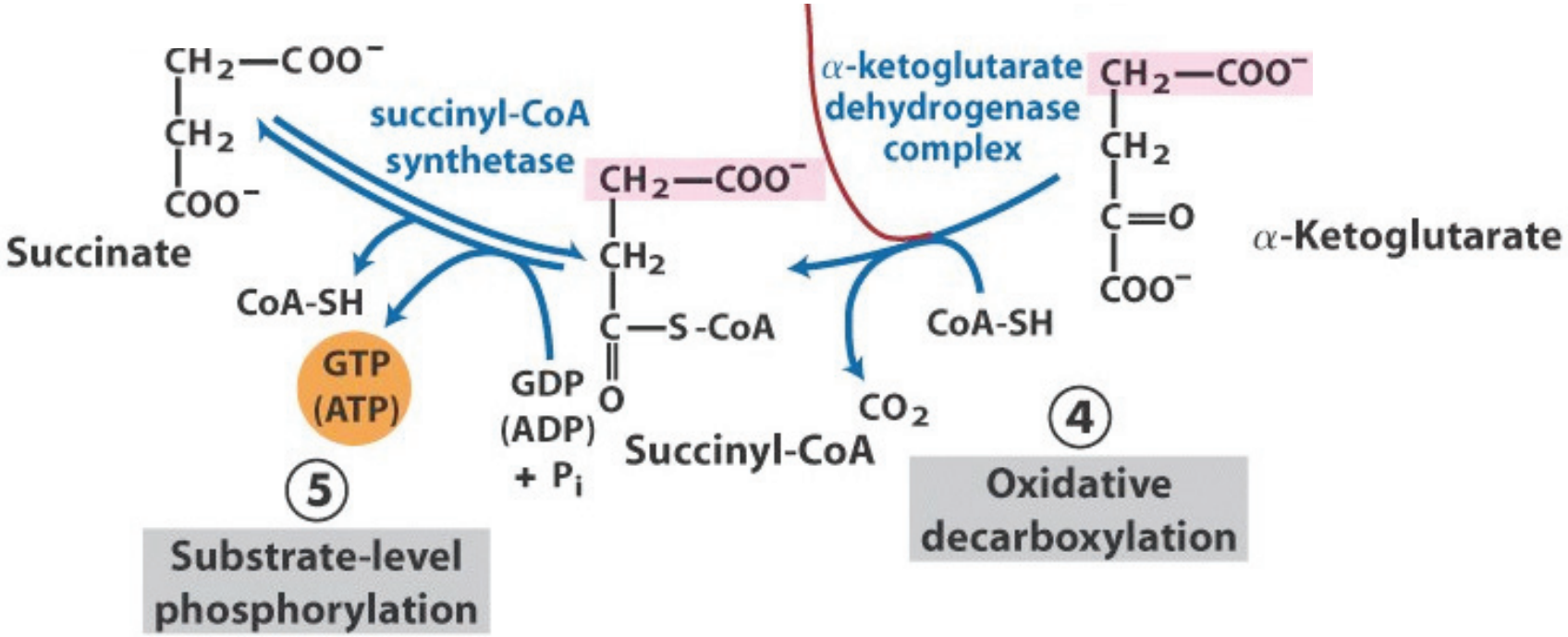


Citric Acid (Krebs) Cycle

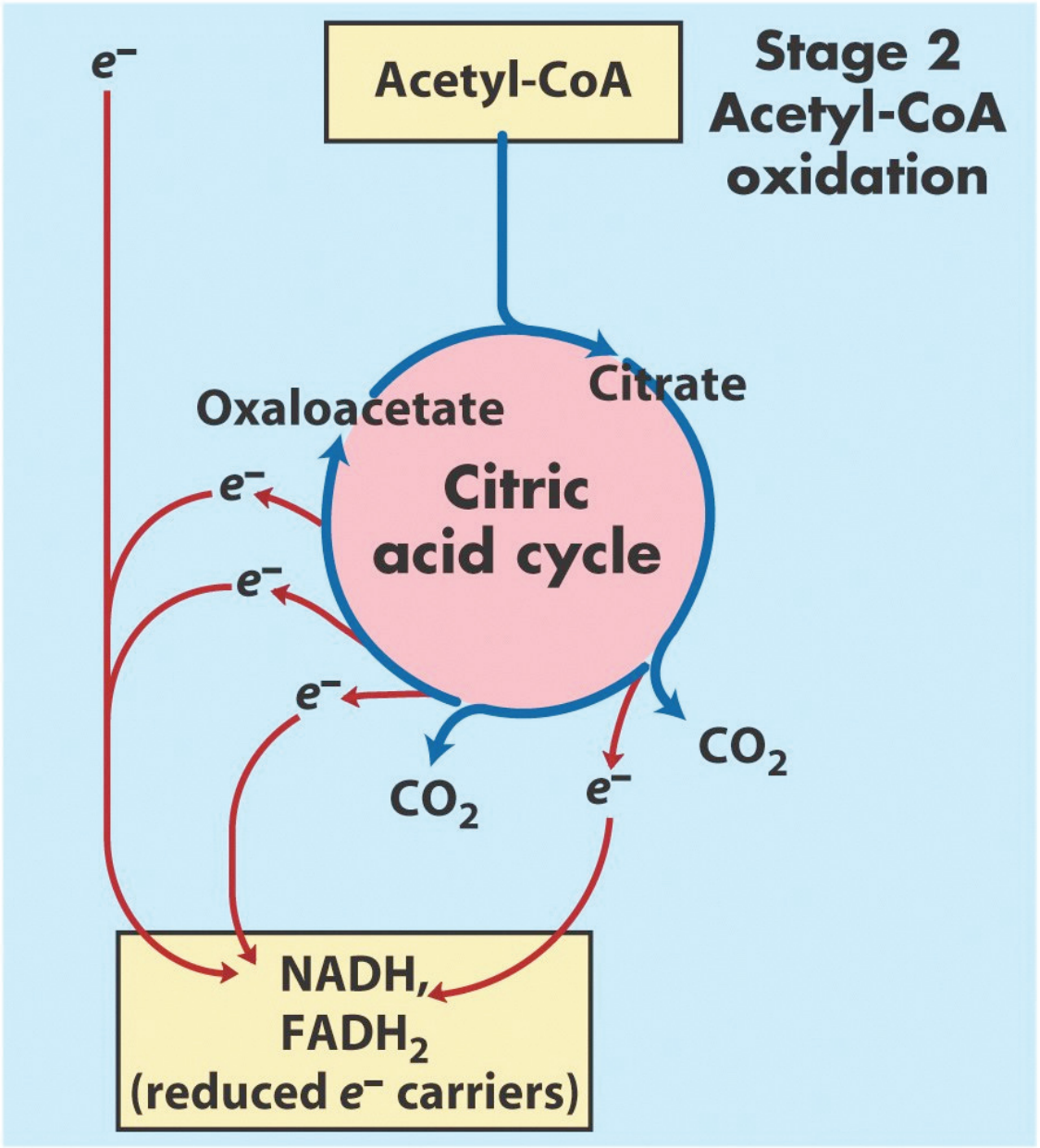


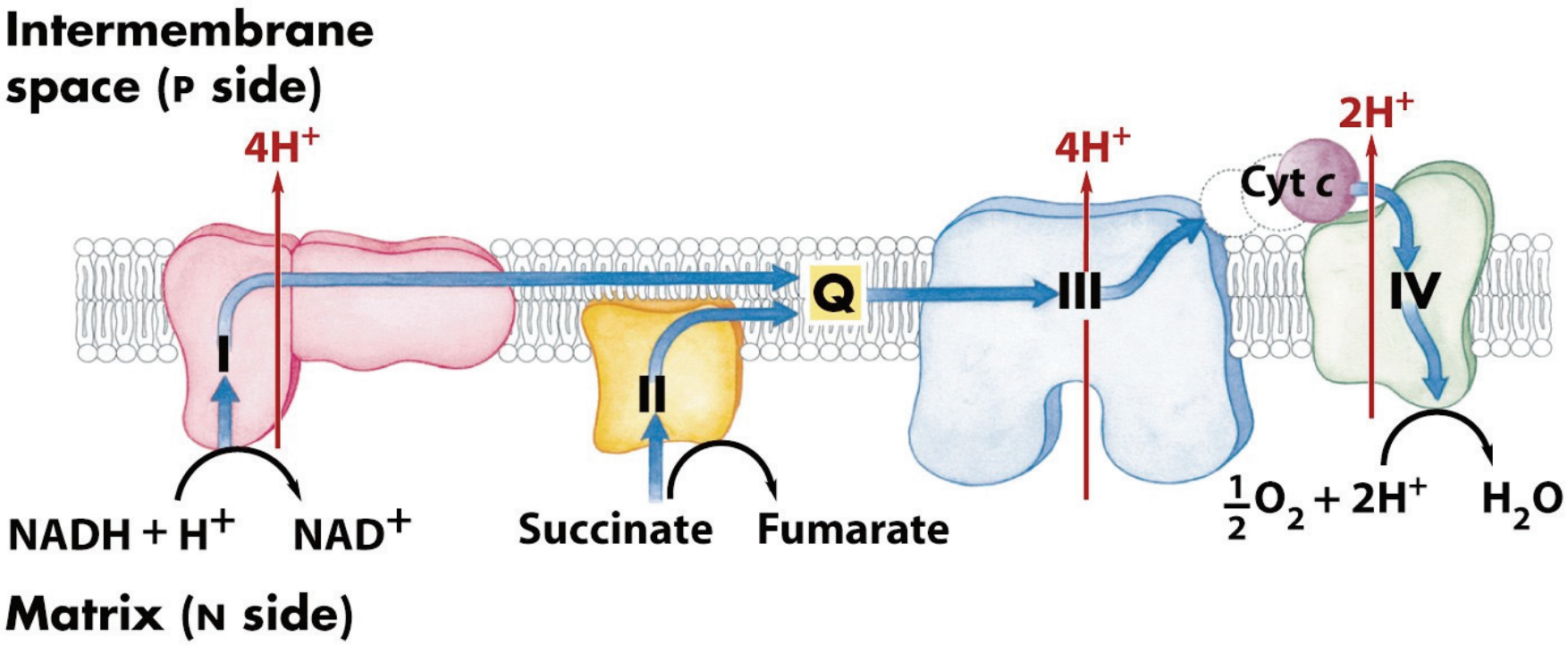


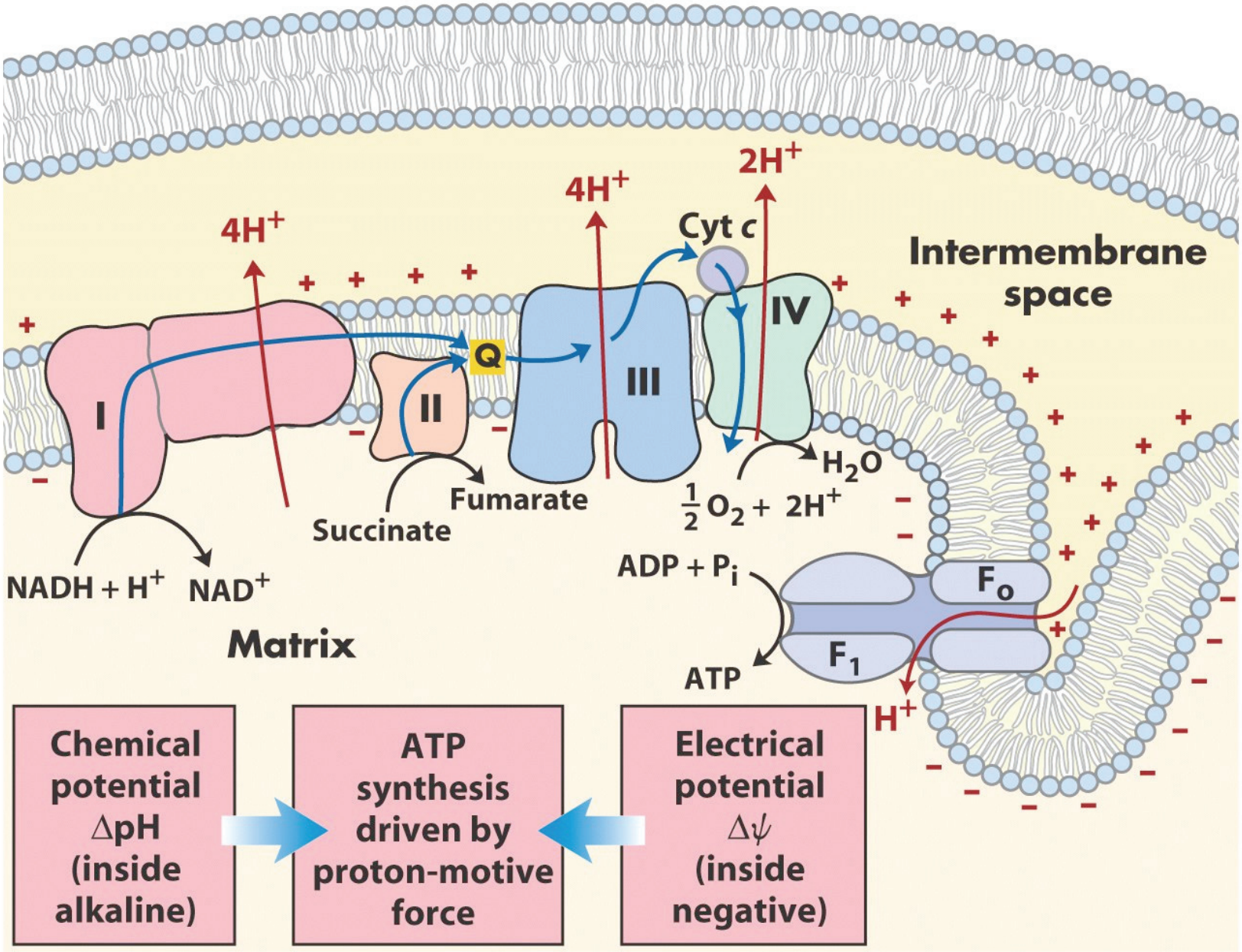
Chapter 18.5E (p 469)



Chapter 18.5E (p 469)


Stage 2
Acetyl-CoA
oxidation
Acetyl-CoA
e⁻
Citrate
Oxaloacetate
Citric
acid cycle
e⁻
e⁻
e⁻
CO2
CO2
e⁻
NADH,
FADH2
(reduced e⁻ carriers)


Intermembrane space (P side)
4H+
4H+
2H+
Cyt c
Q
I
II
III
IV
NADH + H+
NAD+
Succinate
Fumarate
½O2 + 2H+
H2O
Matrix (N side)


4H+
4H+
2H+
Cyt c
Intermembrane space
IV
III
II
I
Q
H2O
½ O2 + 2H+
Fumarate
Succinate
NADH + H+
NAD+
Matrix
ADP + Pi
Fo
F1
ATP
H+
Chemical potential ΔpH (inside alkaline)
ATP synthesis driven by proton-motive force
Electrical potential Δψ (inside negative)