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Biochemistry 5700
Fall, 2001
Exam 3

INSTRUCTIONS:

Do not begin until 10:30 AM. The exam should have 8 questions and 6 pages. Good Luck!!

Equations: $\Delta G' = \Delta G^{\circ\prime} + RT \ln Q$ $\Delta E' = \Delta E^{\circ\prime} - \frac{RT}{nF} \ln Q$ $\Delta G' = -nFE'$

Constants: F = 96.5 kJ/V•mol R = 8.3144 J/mol•K

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(1) 30 points Pot pourri of definitions.

Name a high energy compound from central metabolism that is an acylphosphate	1,3- diphosphoglycerate
Name a high energy compound from central metabolism that is an enol phosphate	phosphoenolpyruvate
Name an enzyme that can discriminate prochiral groups	aconitase
What is the general name for enzymes that transfer a phosphoryl group to water?	phosphatase
What is the general name for enzymes that transfer a phosphoryl group from ATP to an organic acceptor?	kinase
Name a specific enzyme from the citric acid cycle that catalyzes substrate level phosphorylation	succinyl-CoA synthetase
Name a specific enzyme that catalyzes a nonoxidative decarboxylation reaction	pyruvate decarboxylase
What compound is formed from pyruvate reduction when O_2 is limiting in the muscle?	lactate
Name an allosteric effector of liver gycogen phosphorylase glucose	[redacted] glucose
What are the products of glucose oxidation by the oxidative pentose phosphate pathway?	Ribulose-(or ribose-) 5-phosphate + CO_2
What is the final product of beta-oxidation of an odd-chain saturated fatty acid?	propionyl-CoA
What molecule is the initial electron acceptor of the pyruvate dehydrogenase enzyme complex?	lipoamide ox
How many net ATP are synthesized by the reactions of glycolysis?	2
Name a dehydrogenase that uses FAD rather than NAD+ as electron acceptor.	succinate dehydrogenase, acyl-CoA dehydrogenase
What compound is exhaled in the breath of diabetic individuals?	acetone

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(2) (6 points) How does biochemical standard state differ from chemical standard state?

pH = 7 ($[H^+] = 10^{-7}$ M) rather than $[H^+] = 1$ M

(3) (6 points) Given that the reduction potential of the acetoacetate/β–hydroxybutyrate half reaction is –0.346 V and that the reduction potential of the NAD+/NADH half reaction is –0.32 V, write the chemical equation IN THE CORRECT DIRECTION for the reaction catalyzed by β–hydroxybutyrate dehydrogenase starting at standard state conditions.

$NAD^+ + 2e^- + H^+ \longrightarrow NADH \quad E^{o'} = -0.32V$

$2H^+ + CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O^- + 2e^- \longrightarrow CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-COO^- \quad E^{o'} = -0.36$

Add rxns such that $E^{o'}$ is positive for whole rxn:

$\beta\text{-HB} + NAD^+ \longrightarrow AcAc + NADH + H^+ \quad E^{o'} = +0.04$

(4) (6 points) The synthesis of fatty acyl-CoA from a fatty acid and HSCoA requires ATP and proceeds through a fatty acyl-AMP intermediate. Explain why the intermediate is an acyl-AMP rather than an acylphosphate.

The energy required to synthesize a fatty acyl-CoA from free acid + HSCoA is ~ +31 kJ/mol. This is same ΔG as for ATP hydrolysis. Thus, to drive rxn an acyl-AMP intermediate is formed; the other product, PPi, can be hydrolyzed by a pyrophosphatase to drive rxn to right:

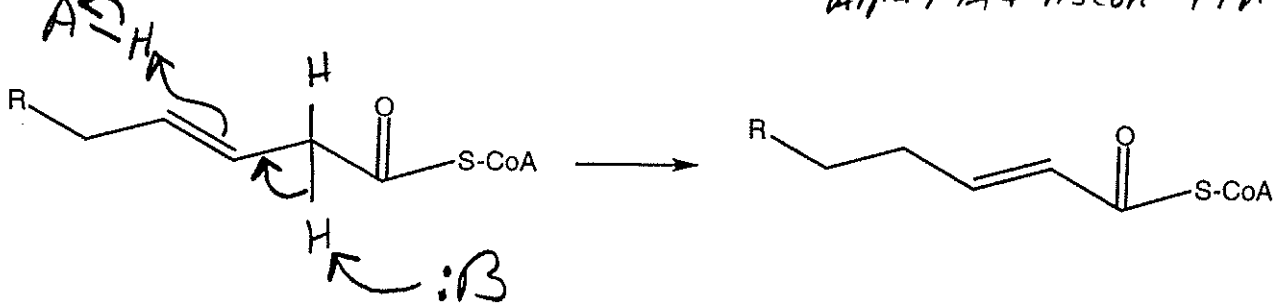
FA + ATP → FA-AMP + PPi

FA-AMP + SCoA → FA-SCoA + AMP

PPi → 2 Pi

ATP + FA + HSCoA → FA-SCoA + AMP + 2 Pi

(5) (6 points) Add the necessary electron pushing arrows, atoms (e.g. ~~hydrogens~~) and general acids/bases to show the mechanism of the following transformation.



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(6) (15 points) For each of the cofactors listed below, name a catabolic enzyme that uses that cofactor and write the balanced equation for that reaction

(1) biotin

propionyl- CoA carboxylase

propionyl- CoA + ATP + HCO_3^- → methylmalonyl-CoA + ADP + Pi

(2) coenzyme B12

methylmalonyl- CoA mutase

Methylmalonyl- CoA → succinyl- CoA

(3) $NADP^+$

glc-6-(P) dehydrogenase

OR glc-6-(P) + $NADP^+$ → NADPH + H^+ + 6-phosphoglucono-δ-lactone

6-phosphogluconate dehydrogenase

6-phosphogluconate + $NADP^+$ → ribulose-5-(P) + H^+ + NADPH + CO_2

(4) Lipoic acid

Pyruvate dehydrogenase (or 1 of the constituent enzymes i.e dihydrolipoyl DH or dihydrolipoyl transacetyl.

Pyruvate + NAD^+ + HSCoA → CO_2 + NADH + Acetyl- CoA

(5) zinc

alcohol DH

ethanol + NAD^+ ⇌ acetaldehyde + NADH + H^+

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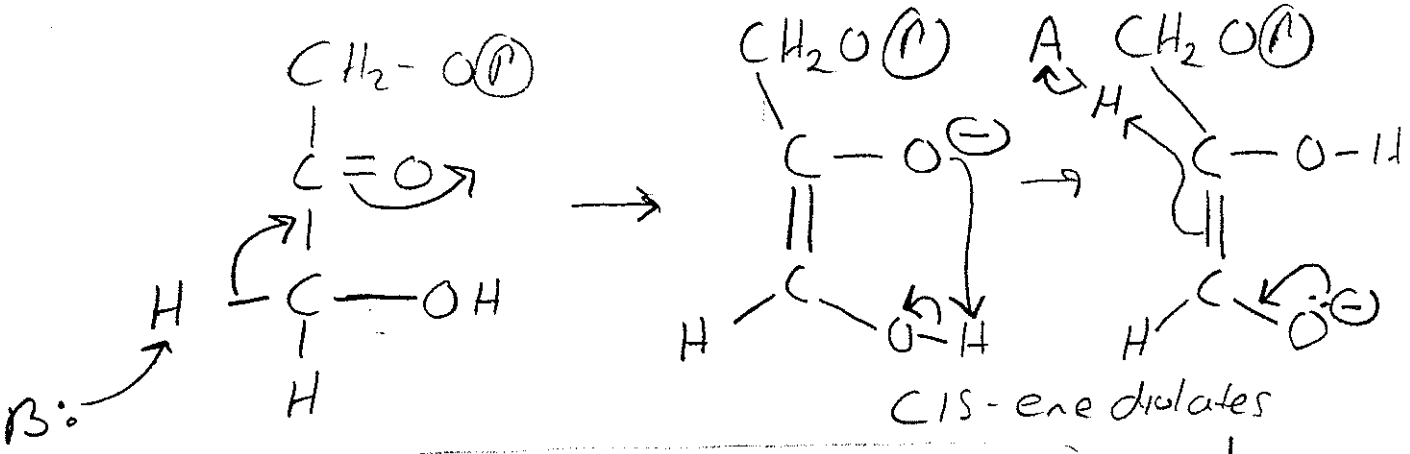
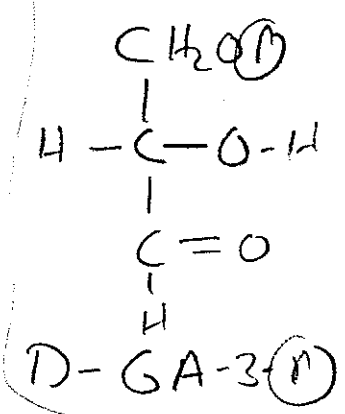
(7) (10 points) Answer **EITHER ONE** of the two questions below- **YOU CHOOSE WHICH ONE:**

Draw a complete mechanism for the isomerization of dihydroxyacetone phosphate to glyceraldehyde-3-phosphate. Push all electrons properly, show all necessary general acids/bases and intermediates.

OR

Describe the series of events involved in the hormonally-controlled mobilization of stored glycogen for use as an energy source (i.e. describe what happens from the time of hormone production and release from the adrenal gland).





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(8) (21 points) Some anaerobic bacteria are able to grow by the fermentation of acetaldehyde to acetate and ethanol.

(a) Write the **complete balanced** chemical equation for the fermentation of 2 acetaldehydes to produce one ethanol and one acetate (if you need the structures of these compounds I will put them on the board).

(b) Given that E°' = -0.197 V for the acetaldehyde/ethanol couple, and E°' = -0.581 V for the acetate/acetaldehyde couple, what is ΔG°' for the fermentation of acetaldehyde?

(c) At a certain point during the fermentation, you determine that the concentration of acetaldehyde in the culture is 5 mM, and the concentrations of ethanol and acetate are each 0.15 mM. At this exact point, how many ATP can be theoretically made per acetate formed from acetaldehyde? (Assume ΔG' = -31 kJ/mol for ATP hydrolysis, T=25°C and the pH is maintained at 7.0).

1/2 rxns:

$2H^+ + CH_3-\overset{O}{\overset{\|}{C}}-H + 2e^- \longrightarrow CH_3-CH_2-OH \quad \mathcal{E}^{o\prime} = -0.197$

$3H^+ + CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} + 2e^- \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O \quad \mathcal{E}^{o\prime} = -0.581$

reverse 2nd 1/2 rxn & add to first 1/2 rxn:

$2H^+ + CH_3-\overset{O}{\overset{\|}{C}}-H + 2e^- \rightarrow CH_3-CH_2OH \quad -0.197V$

$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O \rightarrow 2H^+ + CH_3-\overset{O}{\overset{\|}{C}}-O^- + 2e^- \quad +0.581$

a) $2\,CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O \rightarrow CH_3-CH_2-OH + CH_3-\overset{O}{\overset{\|}{C}}-O^- + H$

$\mathcal{E}^{o\prime} = +0.384$

b) $\Delta G^{o\prime} = -nF\mathcal{E}' = -(2)\left(96.5\frac{kJ}{mol\,eV}\right)(0.384V)$

$= \boxed{-74.1\,kJ/mol}$

c) $\Delta G' = \Delta G^{o\prime} + RT \ln \dfrac{[CH_3-CH_2-OH]\left[CH_3-\overset{O}{\overset{\|}{C}}-O^-\right]}{\left[CH_3-\overset{O}{\overset{\|}{C}}-H\right]^2}$

$\Delta G' = -74.1\,kJ/mol + \left(8.3144\frac{J}{mol\,K}\right)(298K)\left(\frac{1kJ}{1000J}\right)\ln$

$\Delta G' = -91.5\,kJ/mol \qquad \dfrac{(0.15\times10^{-3})(0.15\times10^{-3})}{(5\times10^{-3})^2}$

$\dfrac{-91.5\frac{kJ}{mol\,Acetate}}{-31\,kJ/mol\,ATP} = \boxed{2.95\frac{ATP}{acetate}}$