Sugars as the optimal biosynthetic carbon substrate of aqueous life throughout the Universe

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Abstract: Our previous analysis of the energetics of metabolism showed that both the biosynthesis of amino acids and lipids from sugars, and the fermentation of organic substrates, were energetically driven by electron transfer reactions resulting in carbon redox disproportionation (Weber 1997). Redox disproportionation -- the spontaneous (energetically favorable) direction of carbon group transformation in biosynthesis -- is brought about and driven by the energetically downhill transfer of electron pairs from more oxidized carbon groups (with lower half-cell reduction potentials) to more reduced carbon groups (with higher half-cell reduction potentials). In this report, we compare the redox and kinetic properties of carbon groups in order to evaluate the relative biosynthetic capability of organic substrates, and to identify the optimal biosubstrate. This analysis revealed that sugars (monocarbonyl alditols) are the optimal biosynthetic substrate because they contain the maximum number of biosynthetically useful high energy electrons/carbon atom while still containing a single carbonyl group needed to kinetically facilitate their conversion to useful biosynthetic intermediates. This conclusion applies to aqueous life throughout the Universe because it is based on invariant aqueous carbon chemistry -- primarily, the universal reduction potentials of carbon groups.

Key words: Metabolism -- Biosynthesis -- Bioenergetics -- Sugars -- Reduction-oxidation -- Origin of metabolism -- Origin of life -- Molecular evolution

1. Introduction

Many biosynthetic pathways start with sugar substrates and continue energetically downhill to yield the building blocks of life -- amino acids, lipids, and nucleotides. To understand the favorable energetics of these synthetic processes, we previously calculated the free energy change for the biosynthesis from sugars of E. coli's amino acids, lipids, and nucleotides (Weber 1997). We found that amino acids and lipids are synthesized by energy-yielding redox disproportionation of sugar carbon. Redox disproportionation is defined as the transfer of electrons between two substrate carbon groups that results in an increase (by 2 oxidation number units per electron transferred) in the distance separating the two carbon groups on the carbon oxidation number scale depicted in Figure 1 in which one-carbon groups are plotted as a function of their formal oxidation number (Abeles et al. 1992a) on the abscissa, and their number of carbon-carbon bonds on the ordinate. Overall, redox disproportion of sugar carbon accounted for 84% and 96% (and ATP only 6% and 1%) of the total energy of the biosynthesis of amino acids and lipids, respectively. The energy yields of organic fermentation reactions were also shown to be directly proportional to the degree of carbon redox disproportionation. Fermentation of the sugar, glucose, yielded more energy (9.5-14 kcal/mol) than any other multi-carbon organic substrate. Redox disproportionation of sugar carbon was also shown to provide the energy for the thiol-dependent abiotic synthesis of amino acids from formaldehyde, glycolaldehyde, and ammonia (Weber 1998).

Although the studies discussed above showed that sugars are good substrates for the biotic and abiotic synthesis, they did not identify the optimal biosynthetic substrate. In this report, we compare the redox and kinetic properties of carbon groups in order to evaluate the relative biosynthetic capability of organic substrates, and to identify the optimal biosubstrate of life throughout the Universe. The following analysis of the relative capability of biosubstrates, being based on aqueous thermodynamic measurements, applies only to aqueous life whose metabolism operates in the presence of water.

2. Methods

As shown below for the >C=O/>CHOH half-cell, the standard half-cell potentials in Figure 2 were determined by first estimating the standard free energy (kcal/mol) of reactions describing the reduction of each carbon group (molecule) by hydrogen

(pH 7, 25°C) using the estimation method of Mavrovouniotis (1990, 1991) and energy values of Thauer et al. (1977). The free energy value of each reaction was then converted to mV units using the relationship that a difference of 100 mV corresponds to a free energy change of -4.6 kcal/mol at pH 7 and 25°C (Zubay 1983a). Next, each reaction was expressed as two half-cell equations in the direction of reduction. From the energy of reaction ($\Delta E'_0$) the direction of electron transfer between the two half-cells was established and the two half-cells assigned electron donor and acceptor roles. Knowing the energy of reaction ($\Delta E'_0$) and the standard reduction potential of the hydrogen half-cell at pH 7 (E_0' = - 421 mV), the unknown standard reduction potential of the half-cell was calculated using the relationship: $\Delta E'_0$ (reaction) = E'_0 (acceptor) - E'_0 (donor) (Zubay 1983a). As shown below, this method yielded an (E'_0) value of -212 mV for the >C=O/>CHOH half-cell.

Carbonyl group reduction by H_2 (pH 7, 25°C):

$>C=O + H_2$ -----> $>CHOH$ [$\Delta G^{\circ\prime}$ = - 9.6 kcal/mol, $\Delta E'_0$ (reaction) = +209 mV]

Half-cell equations:

$2H^+ + 2e^-$ -----> H_2 [E'_0 ($2H^+/H_2$) at pH 7 = - 421 mV]

$>C=O + 2H^+ + 2e^-$ -----> $>CHOH$ [E'_0 (>C=O/>CHOH) at pH 7 unknown]

Calculations:

$\Delta E'_0$ (reaction) = E'_0 (>C=O/>CHOH (acceptor)) - E'_0 ($2H^+/H_2$ (donor))

or E'_0 (>C=O/>CHOH) = $\Delta E'_0$ (reaction) + E'_0 ($2H^+/H_2$)

E'_0 (>C=O/>CHOH) = $\Delta E'_0$ (+209 mV) + E'_0 (- 421 mV)

E'_0 (>C=O/>CHOH) = - 212 mV

3. Results and Discussion

The following evaluation of the biosynthetic capability of organic substrates is based on the redox and kinetic properties carbon groups. Redox properties of carbon groups are important because they determine favorable energetics and direction of electron transfer in biosynthetic redox disproportionation. Figure 2 shows the half-cell couples of carbon groups plotted as a function of their formal oxidation numbers on the abscissa, and their standard half-cell potentials on the ordinate. As shown in the figure, the half-cell couples containing more oxidized carbon groups (with higher oxidation numbers) are stronger reductants (with lower reduction

potentials) than half-cell couples containing more reduced carbon groups (with higher reduction potentials). This systematic difference in potential drives electron pair transfer from more oxidized carbon groups that are strong reductants to more reduced groups that are weaker reductants. In other words, the reduction potentials of carbon groups favor the oxidation of more oxidized carbon and the reduction of more reduced carbon. This energetically favored transfer of electrons from more oxidized to more reduced carbon groups brings about, and makes ***redox disproportionation, the Universal spontaneous (energetically favorable) direction of carbon group transformation in chemical and biological processes when electron pair transfer is confined to carbon groups.***

The above discussion shows that biosynthetic carbon transformations are driven by the energetically favorable transfer high energy electron pairs from carbon half-cell couples of lower potential to carbon half-cell couples of higher potential. Therefore, carbon groups that are capable of donating a greater number of high energy electron pairs have the potential to drive a greater number of carbon transformations. From this redox perspective, the optimal biosubstrate would have the highest reduction capacity, that is, be capable of yielding the greatest number of high energy electron pairs/carbon atom (from half-cells of low potential generated by successive dehydrogenation). Viewed this way, the optimal biosubstrate functions like an optimal battery by generating the largest number of high energy electrons per unit mass of storage material. The substrate's reservoir of high energy electrons also protects against depletion of reducing equivalents and buffers changes in the intracellular redox potential. As stated by de Duve (1991) "electrons of high energy level are the true fuel of life".

Figure 3 shows the half-cell couples obtained from internal and terminal carbon groups by successive dehydrogenation. In all cases, the half-cell couple of the first internal carbon group was made accessible by decarboxylation of an arbitrarily chosen terminal carboxylic acid group. The actual biochemical half-cell potentials are the same as in the figure, except that dehydrogenation of the >CHOH/>C=O couple in biological systems is sometimes coupled to decarboxylation giving it a lower potential (see Fig. 3 caption). As shown in the Figure 3 there are only three types of internal carbon groups -- the ketone (>C=O), the alcohols (>CHOH & ≥COH) and the hydrocarbons (>CH_2, ≥CH & >C<). Of the three types of internal groups, the alcohols have the best biosynthetic capability, because they can donate two biosynthetically useful high energy electron pairs/carbon atom from two half-cell couples of low potential (≥ -212 mV (see figure caption), and -573 mV). Although a

carbon-carbon bond must be cleaved for tertiary alcohols to yield two high energy electron pairs, this could occur in branched sugars by retroaldolization. For comparison, the ketone group can donate only one high energy electron pair/carbon from a single half-cell couple of low potential (-573 mV), and the hydrocarbon groups cannot donate any electron pairs because their half-cell potentials (-26 mV) are higher than the potentials of all non-hydrocarbon electron donor groups. Useful high energy electrons can be obtained from hydrocarbons only after oxidation by a strong oxidant like molecular oxygen ($H_2O/0.5\ O_2$, +816 mV, Loach 1976) as in fatty acid oxidation via the TCA cycle (Zubay 1983b). In addition, the ketone group being the most oxidized carbon group containing two carbon-carbon bonds (see Figure 1) cannot act directly as an electron pair donor; it must first be converted to an aldehyde group -- a process that requires cleavage of a substrate carbon-carbon bond. This obligatory cleavage of a carbon-carbon bond further decreases the synthetic capability of the ketone group compared to the hydroxyl group.

Figure 3 also shows the half-cell potentials of the four terminal carbon groups: carboxylic acid, aldehyde, primary alcohol, and primary hydrocarbon. Of these four groups the primary alcohol (or hydroxymethyl group) has the best biosynthetic capability, because it possess two biosynthetically useful high energy electron pairs/carbon from two half-cell couples of low potential ($\geq$ -208 mV and -573 mV). For comparison, the aldehyde group can donate only one high energy electron pair/carbon from a single half-cell couple of low potential (-573 mV); the terminal hydrocarbon group cannot donate any electron pairs for biosynthesis because its half-cell potentials (+40 mV) is higher than the potentials of all non-hydrocarbon electron donor groups; and the carboxylic acid simply has no electron pairs to donate. Therefore, from a redox (thermodynamic) perspective, alditols (sugar alcohols) which contain both internal alcohol groups (>CHOH & $\geq$COH) and terminal alcohol groups ($-CH_2OH$) are the best biosynthetic substrates, because they have the highest reduction capacity -- the largest number of biosynthetically useful high energy electron pairs/carbon. Using the battery analogy, alditols have the largest storage capacity of high energy electrons per unit mass of storage material.

Although the biosynthetic capability of a carbon substrate is determined mainly by its redox properties (the number of high energy electrons/carbon atom), the kinetic behavior of a substrate must also be considered in evaluating its biosynthetic capability. Since biosynthesis requires numerous chemical intermediates, the optimal substrate would certainly contain any chemical group that facilitates its conversion to a variety of intermediates of different size and composition. Of all the

carbon groups, only the carbonyl group (ketone and aldehyde groups), strongly promotes substrate transformations needed to make intermediates of varying size and composition. Most importantly, the carbonyl group strongly facilitates the reversible making and breaking of carbon-carbon bonds necessary for the synthesis of intermediates of varying size. The carbonyl group does this by both supplying the electrophilic carbon, and stabilizing the anionic character of the adjacent nucleophilic carbon (β-activation) involved in carbon-carbon bond formation and cleavage, as in aldolization-retroaldolization reactions (Abeles et al. 1992b, Reeves, 1966, Harsch et al. 1984). In sugars the site of aldol cleavage can move when the carbonyl group interchanges with an adjacent alcohol group (Speck 1958, Abeles, et al. 1992c). Furthermore, carbonyl groups facilitate structural modification of intermediates through β-activation that strongly promotes hydration-dehydration and carboxylation-decarboxylation reactions (Feather and Harris 1973, Abeles et al. 1992d, Abeles et al. 1992e). These beneficial kinetic effects of ketone and aldehyde groups are used widely throughout metabolism to facilitate biochemical transformations (Eisenberg 1966). Therefore, given the strong positive effect of ketone and aldehyde groups on the kinetics of substrate conversion to essential intermediates, the optimal biosubstrate would undoubtedly contain at least one carbonyl group. The large gain in the kinetic facilitation of substrate transformation by the carbonyl group is well worth the small thermodynamic loss (one of thirteen high energy electron pairs) that results from substituting one carbonyl group for an alcohol group in a 6-carbon alditol substrate (hexitol) to give a 6-carbon sugar (hexose) substrate.

However, adding more than one carbonyl group to an alditol substrate does not confer any additional kinetic advantage. It only further lowers the substrate's biosynthetic capability by decreasing both its number of high energy electron pairs/carbon and its ability to reversibly make and break carbon-carbon bonds. Moreover, the general kinetic instability (reactivity) of dicarbonyl and polycarbonyl compounds make them unattractive biosynthetic substrates (Theander 1962, Rubin 1975). For example, dicarbonyl sugars and their polysaccharide-like polymers are chemically degraded much more rapidly than monocarbonyl sugars and their polysaccharides (Theander 1962). Dicarbonyl and polycarbonyl compounds are also predisposed to irreversible nucleophilic addition of ammonia (or amines) that yields heterocyclic compounds (Grimmett and Richards 1965, Grimmet 1965), cleavage reactions (Grimmet 1965, Fisher 1991), and benzilic type rearrangements (Whistler 1960, Rubin 1975, Luengo et al. 1993). ***Therefore, we conclude that sugars***

(monocarbonyl alditols) are the optimal biosynthetic substrate because they contain the maximum number of high energy electrons/carbon atom while still possessing one carbonyl group needed to kinetically facilitate their conversion to a variety of useful biosynthetic intermediates. This conclusion applies to aqueous life throughout the Universe, because it is based on invariant aqueous carbon chemistry -- primarily the universal reduction potentials of carbon groups.

In the foregoing analysis, only organic substrates containing carbon, hydrogen, and oxygen were evaluated for their biosynthetic capability. Substrates containing heteroatoms were not considered, because the initial biosynthetic reactions (cleavage, elimination and redox reactions) needed to generate essential biosynthetic intermediates would lead to replacement of most carbon-bonded heteroatoms (like -SH, $-NH_2$) with oxygen (-OH). This expected early loss of heteroatoms could explain why central metabolic pathways use only intermediates containing carbon, hydrogen and oxygen. Also, unsaturated and aromatic carbon groups were not evaluated, because (a) unsaturated substituted carbon groups (enols (=CHOH,=COH-) and ketenes (=C=O) are unstable to ketonization (Forsen and Nilsson 1970) and hydrolysis (Blake 1980, Allen and Tidwell 1987), respectively; (b) unsaturated and aromatic hydrocarbon groups ($=CH_2$, =CH-, =C=), like their saturated counterparts discussed earlier, are weak reductants incapable of acting as electron donors in biosynthesis; and (c) substituted aromatic carbon groups (phenols (=COH-) and aromatic ketones (>C=O)) have fewer high energy electron pairs/carbon than their saturated counterparts, and require ring opening to be converted to a variety of biosynthetic intermediates.

4. Relevance to the Origin of Life

The same properties that make sugars the optimal biosynthetic substrate also make sugars very attractive substrates for chemical transformations leading to the origin of life. First, the high energy electrons in sugars can drive not only biological, but also prebiotic chemical transformations of sugars resulting in carbon redox disproportionation. This chemical disproportionation of sugars is best exemplified by the conversion of glyceraldehyde to lactic acid that occurs by dehydration of glyceraldehyde to pyruvaldehyde which undergoes intramolecular hydride transfer yielding lactic acid (Weber 1987, ref. therein). In the presence of a thiol some of the energy of the disproportionative conversion of pyruvaldehyde (an α-ketoaldehyde) to lactic acid (an α-hydroxy acid) can be trapped as the thioester of lactic acid (Weber

1984ab). A similar reaction of glyceraldehdye in the presence of thiol and ammonia has been shown to yield alanine, presumably via alanine thioester (Weber 1985). The second attractive property of sugars is their plausible prebiotic synthesis from formaldehyde in the presence of trace amounts of a second hydroxyaldehyde (Schwartz and de Graaf 1993, ref. therein). Recently, we described a 'one-pot' reaction system capable of both synthesizing sugars and converting sugars to amino acids (Weber 1998). In this reaction system formaldehyde and glycolaldehyde (1- and 2-carbon substrates) condense to give trioses and tetroses (3- an 4-carbon sugars) that, in the presence of ammonia and a thiol, undergo redox disproportionative transformations to give alanine and homoserine. The thiol-dependency of this reaction indicates that amino acid synthesis occurs via amino acid thioester intermediates which are capable of forming peptides (Weber and Orgel 1979)). These experimental studies show that the same thermodynamic and kinetic properties that make sugars the optimal biosynthetic substrate also make sugars a very attractive substrate for the origin of life.

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Figure Legends

Figure 1. Carbon groups and one-carbon molecules positioned according to their formal carbon oxidation number on the abscissa, and their number of carbon-carbon bonds on the ordinate. The dash representing bonds to other carbon atoms can be saturated; unsaturated, or aromatic. The O (oxygen) in carbon groups can be replaced by a heteroatom (N (nitrogen) or S (sulfur)).

Figure 2. Half-cell equations of carbon groups plotted as a function of their formal carbon oxidation number on the abscissa, and their standard reduction potential (mV) on the ordinate. Standard reduction potentials (pH 7, 25°C) of each half-cell equation were calculated as described in the Methods Section.

Figure 3. Standard reduction potentials (mV) of half-cell couples generated by the sequential dehydrogenation of organic substrates starting at an arbitrary carboxylic acid terminus. In the phosphogluconate pathway (Zubay 1983c), the coupling of the >C=O/>CHOH half-cell to decarboxylation lowers its standard reduction potential from - 212 mV to -246 mV, and makes its potential dependent on the aqueous carbon dioxide concentration. Due to these complications the potential of the >C=O/>CHOH half-cell is given as $\geq$ -212 mV.

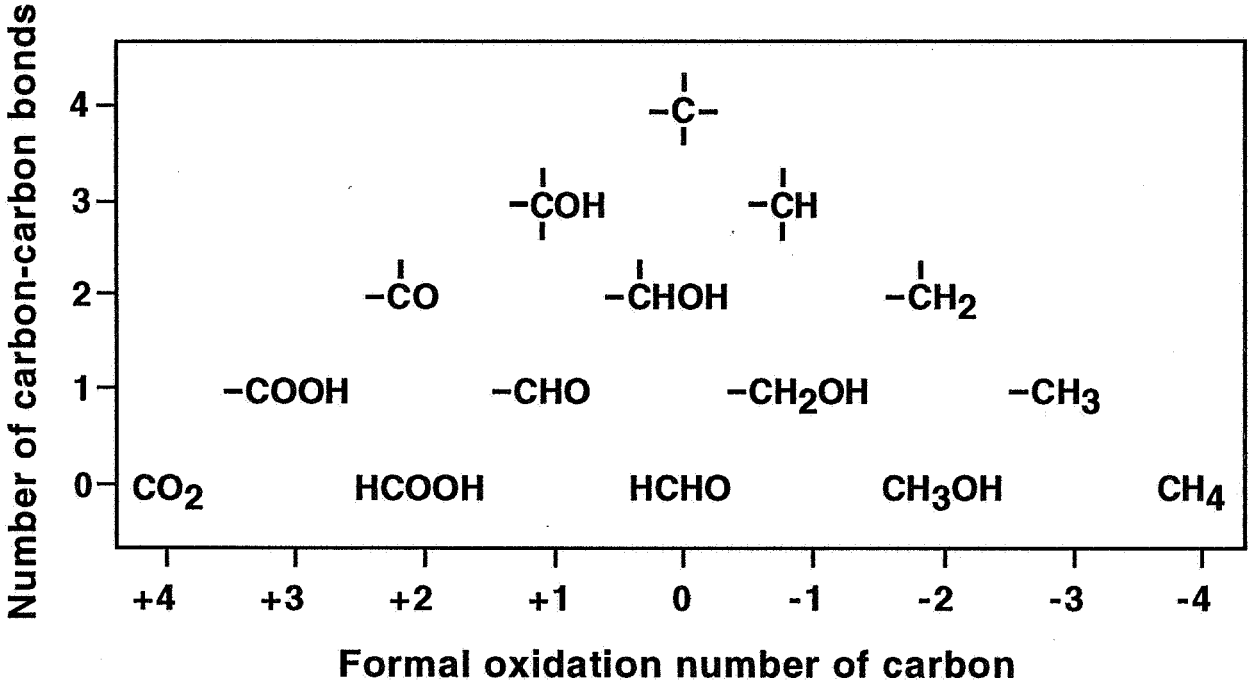

Number of carbon-carbon bonds
4
3
2
1
0
–C–
–COH
–CH
–CO
–CHOH
–CH2
–COOH
–CHO
–CH2OH
–CH3
CO2
HCOOH
HCHO
CH3OH
CH4
+4
+3
+2
+1
0
-1
-2
-3
-4
Formal oxidation number of carbon

Figure 1

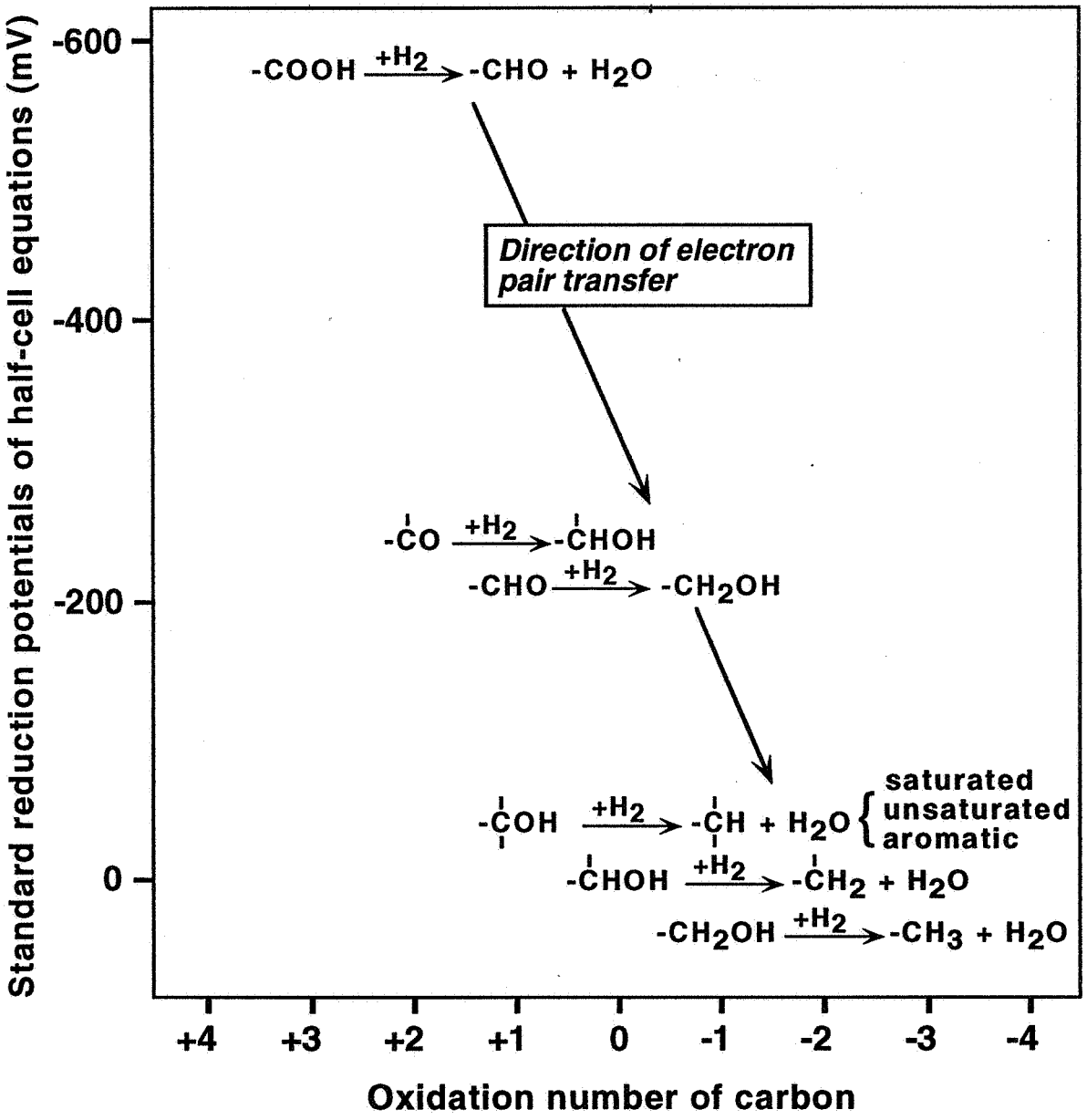
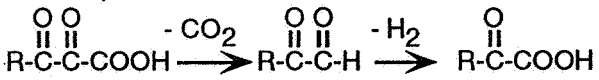

Standard reduction potentials of half-cell equations (mV)
-600
-400
-200
0
-COOH +H2 -CHO + H2O
Direction of electron pair transfer
-CO +H2 -CHOH
-CHO +H2 -CH2OH
-COH +H2 -CH + H2O
saturated
unsaturated
aromatic
-CHOH +H2 -CH2 + H2O
-CH2OH +H2 -CH3 + H2O
+4
+3
+2
+1
0
-1
-2
-3
-4
Oxidation number of carbon

Figure 1

INTERNAL CARBON GROUPS

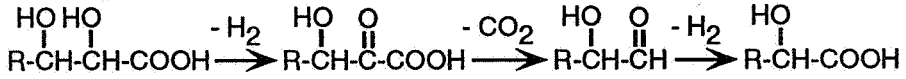
Ketone:

1 useful e^- pair/carbon, -CHO/-COOH = -573 mV



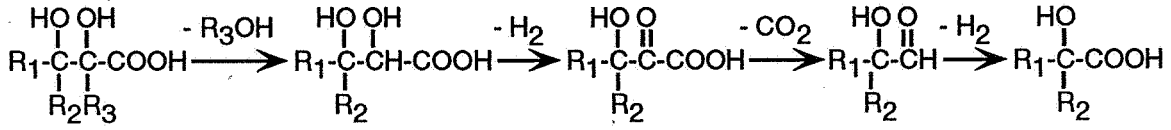
Secondary alcohol:

2 useful e^- pairs/carbon, >CHOH/ >C=O ≥ -212 mV, -CHO/-COOH = -573 mV



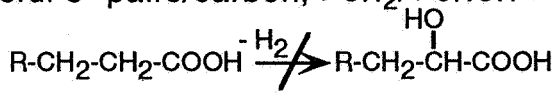
Tertiary alcohol:

2 useful e^- pairs/carbon, >CHOH/ >C=O ≥ -212 mV, -CHO/-COOH = -573 mV



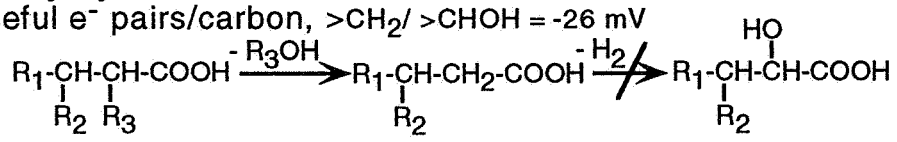
Secondary hydrocarbon:

2 useful e^- pairs/carbon, $>CH_2$/ >CHOH = -26 mV



Tertiary hydrocarbon:

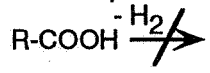
0 useful e^- pairs/carbon, $>CH_2$/ >CHOH = -26 mV



TERMINAL CARBON GROUPS

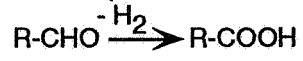
Carboxylic acid:

0 useful e^- pairs/carbon



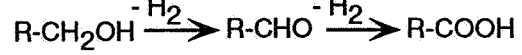
Aldehyde:

1 useful e^- pair/carbon, -CHO/-COOH = -573 mV



Primary alcohol:

2 useful e^- pairs/carbon, $-CH_2OH$/-CHO = -208 mV, -CHO/-COOH = -573 mV



Primary hydrocarbon:

0 useful e^- pairs/carbon, $-CH_3$ /$-CH_2OH$ = +40 mV

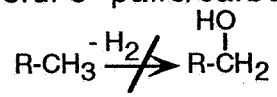


Figure 3