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Title:

Hydrogenation Reactions of Carbon on Earth: Linking Methane, Margarine, and Life

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Abstract

Hydrogenation reactions are a major route of electron and proton flow on Earth. Hydrogenations occupy pivotal points in the Earth's global geochemical cycles, interfacing geology and organic chemistry, and also feature prominently in biological systems. Some examples of hydrogenation reactions on Earth today include the production and consumption of methane in both abiotic and biotic reactions, the reduction of protons in hydrothermal settings, and the biological synthesis and degradation of fatty acids. Hydrogenation reactions were likely important for prebiotic chemistry on the early Earth, and today serve as one of the fundamental reaction classes that enable cellular life to construct biomolecules. An understanding and awareness of hydrogenation reactions is helpful for comprehending the larger web of molecular and material inter-conversions on our planet. In this brief review we detail some important hydrogenation *and* dehydrogenation reactions as they relate to geology, biology, industry, and atmospheric chemistry. Such reactions have implications ranging from the suite of reactions on early Earth to industrial applications like the production of hydrocarbon fuel.

Keywords

Hydrogenation, hydrogen, methane, carbon dioxide, carbon monoxide, redox, reduction, oxidation

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Introduction

Hydrogenation is defined as reduction of a substrate (organic or mineral) by addition of hydrogen. This review surveys some of the key geochemical hydrogenation reactions of carbon on Earth where such reactions are widespread. Deep in the Earth's interior, at high temperatures and pressures, these reactions play important roles in controlling the long-term redox state of the planet. Hydrogenation could have played a role in the prebiotic chemistry of the ancient Earth through precursor reactions akin to how such reactions today enable cellular life to build biomolecules in human biology and the biologic systems of other organisms. Hydrogenation reactions have been of industrial importance since their discovery, finding wide applications ranging from the production of margarine to the use of solar driven CO_2 reduction to form petroleum and in liquid fuel technologies. Although the focus of this review will be carbon hydrogenations, we note that other substrates, such as oxygen, sulfate and nitrogen gas, are also hydrogenated and dehydrogenated in nature. Table 1 shows a few examples. A more complete tabulation of hydrogenation reactions in biology is available in Tables 13 and 14 (Thauer et al. 1977), and a recent review on some topics discussed here has recently appeared (Preiner et al. 2018).

What is a hydrogenation reaction?

The hydrogen involved in a hydrogenation reaction can either come in the form of hydride (H^-), or the hydrogen atom ($H^\cdot$), and is often accompanied by proton addition (H^+). Hydrogenation reactions are categorized by the source of electrons and protons. When molecular hydrogen (H_2) is the source of electron and protons, as is often the case in both geology and industry, the reaction is simply known as “hydrogenation”. When another molecule is the source of electrons and protons, as is often the case in biology, the reaction is known as “transfer hydrogenation”.

A number of relevant hydrogenation reactions are shown in **Figure 1**, which illustrates two pathways of CO_2 reduction (C-1 reactions) as they exist in, and out of biology, as well as some hydrogenation reactions involving more than one carbon atom. Geologic hydrogenation reactions commonly involve simple inorganic oxidized carbon compounds, such as carbon monoxide (CO) or carbon dioxide (CO_2), which react with H_2 to form simple reduced carbon compounds, such as methane (CH_4; “methanation”) or formate (HCO_2^-). Biological enzymes enhance hydrogenation reaction rates by several orders of magnitude. Intriguingly, some of these enzymes use the same metals that facilitate catalysis of the abiotic reaction, such as nickel and iron. Biology also uses transfer hydrogenation reactions to synthesize substrates into sugars, fatty acids and amino acids, using biological cofactors such as nicotinamide adenine dinucleotide (NADH), flavin adenine dinucleotide (FAD), or the iron-sulfur protein ferredoxin as electron releasing reductants instead of H_2.

Rather than only being hydrogenated themselves, carbon compounds can also act as hydrogen donors. For example, the common reductants formic acid and isopropanol can hydrogenate other molecules via transfer hydrogenation, resulting in the formation of CO_2 and acetone, respectively. If the hydrogenation is written as the reduction of an alkene (R-CH=CH-R) to an alkane (R-CH_2-CH_2-R), then in general some species (DH_2) will act as the hydrogen donor. In this formulation, R represents a carbon with unspecified bonding partners, and each line indicates a covalent bond. An example of a hydrogenation reaction is shown below where a carbon-carbon double bond is reduced is outlined in Equation 1.

$$1)\ DH_2 + R\text{-}CH{=}CH\text{-}R \rightleftharpoons R\text{-}CH_2\text{-}CH_2\text{-}R + D$$

The reduction of oxidized fatty acids to margarine is a well-known example of hydrogenation of alkenes to alkanes, where molecular (H_2) is used as the reductant, and the kinked double bond containing alkene fats is converted to more linear alkanes, the so-called saturated fats, which have a greater tendency to gel at room temperature.

Serpentinization: A geological facilitator of hydrogenation

Over the past two decades there has been a profound rise in appreciation of the importance of serpentinization in generating H_2 in a wide range of environmental settings and conditions (see Box 1). The reducing conditions created by serpentinization can facilitate the hydrogenation of dissolved inorganic compounds, such as CO_2, SO_4^{2-}, and NO_3. Hydrogen production, here portrayed in a simplified and generalized reaction

$$2)\qquad 2FeO + H_2O \rightleftharpoons Fe_2O_3 + H_2$$

is tied to the oxidation of ferrous to ferric iron by water. In the above reaction, FeO represents the ferrous iron component in olivine and pyroxene, and Fe_2O_3 represents the ferric iron component in product minerals. While the distribution and valence of iron among serpentine-group minerals (lizardite, chrysotile, antigorite), magnetite, brucite, and talc (in addition to other minor minerals) control the production of H_2, the stability and composition of these minerals depends on protolith composition, alteration temperature, reaction kinetics, and composition of the reactant fluid. Thermodynamic reaction path models are useful to assess how mineral and rock composition affects H_2 production (e.g. (McCollom and Bach 2009; Klein et al. 2013).

Box 1: Serpentinization 101

The alteration of magnesium- and iron-rich rocks by water is commonly referred to as ‘serpentinization’. This process turns a dry, dense, mechanically strong, and reduced rock into a hydrous, significantly less dense, mechanically weak, and strongly oxidized rock mainly composed of serpentine-group minerals. Serpentinization is widespread in marine environments and occurs at mid-ocean ridges, at ridge flanks and fracture zones, at magma-poor rifted plate margins, and in forearc settings of subduction zones. Serpentinization is evident in Archean rocks (komatiites), suggesting that it has been going on throughout most of Earth’s history. Notably, there is evidence from meteorites and remote sensing for serpentinization beyond Earth. The oxidation of iron by water generates molecular hydrogen, which, as a byproduct of serpentinization, is of central importance for hydrogenotrophic microorganisms and the abiotic hydrogenation of carbon compounds to form hydrocarbons.

These models suggest that the production of H_2 during serpentinization of peridotite, the most common ultramafic rock type in Earth's upper mantle, peaks at temperatures of ~300-320°C. At higher temperatures, olivine is part of the equilibrium mineral assemblage, which limits the amount of oxidizable iron available for H_2 generation. At lower temperatures, the amount of oxidizable iron available for H_2 generation is limited by preferential partitioning of ferrous iron in brucite. Hydrothermal laboratory experiments support these findings, however, they highlight that reaction kinetics and hydrodynamic properties must be taken into account to evaluate the underlying processes of serpentinization and associated H_2 production (Martin and Fyfe 1970; Allen and Seyfried 2003; Malvoisin and Brunet 2014; Klein et al. 2015; Lamadrid et al. 2017; Syverson et al. 2017; Escario et al. 2018).

Hydrogen produced during serpentinization can facilitate the abiotic formation of CH_4 and other hydrocarbons via hydrogenation of CO_2. Indeed, vent fluids associated with serpentinization of ultramafic rocks at mid-ocean ridges are commonly enriched in CH_4 and other short-chain hydrocarbons (Charlou et al. 2002; Proskurowski et al. 2008; McDermott et al. 2015; Lang et al. 2018). However, the pathways and conditions of abiotic synthesis reactions remain incompletely understood.

Abiotic synthesis of hydrocarbons

In catalyzed reactions, methane can be formed through hydrogenation reactions, for example:

$$3)\ CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

$$4)\ CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

These reactions have been the focus of extensive research and technological development in chemical engineering since its discovery (Sabatier and Senderens 1902; Rönsch et al. 2016).

Related to the CH_4 forming Sabatier process (Reaction 3 above) is the Fischer-Tropsch type of reaction which produces a range of abiotic hydrocarbons via hydrogenation of CO with H_2. This process can be generalized by the reaction:

$$5)\ (2n + 1)\ H_2 + n\ CO \rightleftharpoons C_nH_{2n+2} + n\ H_2O$$

The relative abundance of CH_4, C_2H_6, C_3H_8 and other compounds follows a probabilistic distribution of molecular lengths, termed the Anderson-Schulz-Flory distribution (Anderson 1978). Together, methanation, and the Fischer-Tropsch type processes have been suggested to explain the origin of CH_4 and other hydrocarbons, however mass balance, stable and radiogenic isotope constraints suggest that dissolved inorganic carbon is not reduced to CH_4 during convection of hydrothermal fluids (McDermott et al. 2015). Accordingly, CH_4 formation is likely decoupled from convecting fluids and may occur, for instance, in fluid inclusions as one of us has recently suggested (Klein et al. 2019).

Regarding interconversions of small carbon compounds in hydrothermal fluids, methane formation occurs without mineral catalysts (Seewald et al. 2006), but the reactions are sluggish, in particular at low temperatures (McCollom 2016). For methanation to be more effective in an aqueous environment, catalysts are needed, often including nickel (Gadalla and Bower 1988; Horita and Berndt 1999; Miao et al. 2016). In these conditions a number of mechanisms may be possible (**Figure 2**). Under hydrothermal conditions, the uncatalyzed reduction of CO_2 to methanol (CH_3OH) proceeds via a stepwise sequence of reactions that involve the formation of formic acid (HCOOH), CO, and possibly formaldehyde (CH_2O), as intermediary reaction products (Seewald et al. 2006). However, kinetic barriers appear to inhibit the reduction of CH_3OH to CH_4 and allow the reaction intermediaries to accumulate in solution at high concentrations reaching metastable thermodynamic equilibrium (Seewald et al. 2006). Indeed, formate appears to form on short timescales during mixing of reducing hydrothermal fluids with seawater, whereas the formation of CH_4 may take thousands of years (Lang et al. 2012; McDermott et al. 2015).

Methane formation appears to be significantly more efficient in the presence of a vapor phase (McCollom 2016). The preferred interpretation for this observation is that abiotic CH_4 synthesis is promoted by the presence of a H_2 vapor phase in direct contact with catalytic mineral surfaces without the interference of water molecules. In reaction fronts in serpentinizing environments, H_2O consumption and H_2 production from serpentinization can lead to H_2 exsolution into a vapor phase, at least at low pressures, as indicated by pentlandite-awaruite-magnetite assemblages found in partially serpentinized rocks (Klein and Bach 2009). Although methanation of CO_2 in a strongly reducing vapor phase seems feasible under specific conditions, radiocarbon data and mass balance constraints suggest that methanation of CO_2 is relatively inefficient during hydrothermal circulation. Alternatively, abiotic CH_4 can be leached from rock surfaces (Welhan 1988) or fluid inclusions (McDermott et al. 2015; McCollom 2016; Wang et al. 2018; Klein et al. 2019). Indeed, Klein et al. (2019) examined 160 olivine-bearing gabbros and peridotites from a wide range of geologic settings and found H_2 and abiotic CH_4 coexisting with serpentine, brucite, and magnetite within olivine-hosted secondary fluid inclusions in most of their samples. They estimated that fluid inclusions may store as much as 5 Pg of CH_4 in oceanic crust and mantle formed at slow and ultraslow spreading ridges. The proposed pathways of CH_4 formation in olivine-hosted fluid inclusions is as follows: Carbon-bearing aqueous fluids are trapped as secondary inclusions in olivine between ~ 800 and 400 °C and react with their olivine host upon cooling below 340 °C, which results in the formation of serpentine, brucite, magnetite, and H_2. The production of H_2 and concomitant consumption of liquid water by precipitation of hydrous minerals inside the inclusion creates conditions conducive to CO_2 reduction to CH_4. While CH_4 and H_2 can be stored over geological timescales within these inclusions, gases can be released during dissolution or fracturing of the olivine host. Remarkably, the stable isotope compositions of CH_4 in vent fluids emanating from mafic- and ultramafic-hosted hydrothermal systems are virtually indistinguishable, calling for a common underlying process of CH_4 formation (Wang et al. 2018). Because CH_4-rich secondary fluid inclusions occur in olivine-bearing mafic and ultramafic rocks, they represent a common source of abiotic CH_4 in both mafic- and ultramafic-hosted hydrothermal systems (Klein et al. 2019).

Collectively, abiotic hydrocarbon formation comprises a substantial carbon flow in submarine hydrothermal systems, continental gas seeps and alkaline springs, and even on other planetary bodies such as Mars and Enceladus (Horita and Berndt 1999; Charlou et al. 2002; Etiope and Sherwood Lollar 2013; Klein et al. 2019).

Other geologic contexts: Hydrogenation of inorganic metal carbonate

Interaction between metal carbonate minerals and H_2 as shown in Equation 6 may represent an important process in planetary sciences, yet it remains poorly investigated under geological conditions. A comprehensive review on the subject was recently published (Lux et al. 2018).

$$6)\ MeCO_3 + 4H_2 \rightleftharpoons MeO + CH_4 + 2H_2O$$

Experimental investigations have been conducted over a wide range of temperature conditions between 200°C to 900°C, but most commonly at ambient pressure conditions, with the exception of the most recent studies reaching up to about 1.2 Mpa (Baldauf‑Sommerbauer et al. 2016). In a pure hydrogen atmosphere, hydrogenation may occur through different pathways as a function of several parameters including the amount and size of carbonate substratum, the nature of the metals involved, the presence of catalysts, temperature and pressure. In the presence of water, hydrogenation can also happen as a result of thermal decomposition (Perry and Ahmad 1977; McCollom 2003; Tao et al. 2018). In this case, ferrous iron is oxidized to ferric iron in magnetite, generating H_2 from water which subsequently hydrogenates CO_2 to organic compounds.

Although some experimental results appear contradictory from one to another study (see review by Lux et al., 2018), the aforementioned parameters influence the amount and rates of carbonate decomposition, as well as on the speciation of the produced fluid phase, with large deviations from the general equation reported above. The most common alkaline-earth metal carbonates calcite and dolomite ($CaCO_3$, $MgCO_3$) tend to produce CO_2 and CO relative to CH_4 or heavier hydrocarbons in the absence of catalysts such as Ni, Ir, Pd and Co (Padeste et al. 1991; Reller et al. 1991; Yoshida et al. 1999; Baldauf-Sommerbauer et al. 2016). Transition metal carbonates, such as siderite ($FeCO_3$), may produce CH_4 during redox reactions involving Fe, or the catalytic effect of native metal/oxides forming during the carbonate dissociation (Giardini and Salotti 1969; Reller et al. 1991; Tsuneto et al. 1992). Both direct carbonate methanation, i.e. direct surface-gas reaction between carbonate minerals and H_2 to form light molecular weight hydrocarbons such as CH_4, and methanation mediated through an intermediate CO_2- or CO-H_2 interaction have been documented (Lux et al. 2018).

Lux et al. (2018) discussed the potential industrial and environmental implications of metal carbonate hydrogenation. Manifestations of these reactions in natural systems are still barely documented. Lazar et al. 2014 discussed the possible implications of carbonate reduction on carbon mobility in subduction zones based on experimental results (2-10 kbar; 300-700 °C in aqueous fluids with changing fO_2) (Lazar et al. 2014). Giardini and Salotti 1969 and Salotti et al.

1971 discussed the potential role of this process on the formation of abiotic light hydrocarbons and solid organic C compounds in the Earth crust and in carbonaceous chondrites (Giardini and Salotti 1969; Salotti et al. 1971). Similarly, carbonate methanation has been proposed as a possible mechanism to produce abiotic CH_4 at relatively high-pressure conditions in subduction zones (0.5-1GPa; ~400 °C) based on natural samples (Vitale Brovarone et al. 2017).

Hydrogenation of reduced C phases in the deep Earth

Hydrogenation/dehydrogenation reactions involving H_2 and reduced C reservoirs, either solid (graphite, diamond and carbides) or fluid (e.g., CH_4), are also proposed to regulate recycling of C in the deep Earth. The equilibrium involving of elemental C, H_2 and CH_4 is classically included among the reactions regulating fluid-rock equilibria involving C, O and H in the so-called COH system (Deines 1980; Connolly 1995), following the reaction:

$$7)\ CH_4 \rightleftharpoons C_x + 2H_2$$

For example, pyrolitic dissociation of CH_4 to form graphite and H_2 was proposed (Salotti et al. 1971) as a mechanism generating massive graphite deposits. The significance of this reaction in geological systems has been questioned based on the rarity of H_2-rich fluids in geological systems (Rumble and Hoering 1986). The reverse reaction, the abiotic generation of CH_4 through C hydrogenation, may occur in graphite-bearing metamorphosed ultramafic rocks percolated by H_2-rich geological fluids (Vitale Brovarone et al. 2017), suggesting that Reaction (7) may be achieved in nature. Furthermore, immiscibility of H_2 in aqueous fluids at upper mantle conditions, as demonstrated by experimental results (Bali et al. 2013), may favor the geological occurrence of H_2-mineral reactions (Griffin et al. 2018). The kinetics of graphite hydrogenation has been extensively investigated in material sciences at low-pressure conditions (Goethel and

Yang 1988). In the deep Earth, the significance and kinetics of these reactions remain barely known. Hydrogenation/dehydrogenation of reduced C phases may extend to higher-pressure conditions and involve diamond or metal carbide precipitation/dissolution. The potential role of CH_4 dehydrogenation on diamond formation through the latter reaction is known (Deines 1980) and might explain the origin of some CH_4-deposited natural diamonds reported in the literature (Thomassot et al. 2007; Smit et al. 2016). Interactions between iron carbides and H^+ are also proposed to produce hydrocarbons (Lai 2007), but the significance of this reaction in deep terrestrial conditions remains unclear.

Hydrogenations concerning iron carbonyls and metal sulfides with relevance to prebiotic chemistry.

Life as we know it links energy released during electron transfer reactions to cell activity, and hydrogenation reactions are a widespread mechanism of this. It has even been suggested that a primary role of life is to hydrogenate CO_2 (Nitschke and Russell 2009). Before the formation of the first cells, hydrogenation reactions would have been important for the formation and interconversion of carbon molecules of intermediate redox states. Since CO_2 reduction involves hydrogenation, it is required for all CO_2-fixing life, and many reactions in modern metabolisms are either hydrogenation or dehydrogenation reactions. The same would likely be true of any early metabolism. Of relevance to primordial CO_2 fixation, the hydrogenation of CO_2 leading to formate/CO could represent a source of reduced carbon compounds, potentially present in geologic environments such as during volcanic outgassing into the deep sea (Cadle 1980). At 0.2 GPa and 250°C, traces of pyruvic acid have been detected in laboratory experiments iron monosulfide (FeS) serving as the reductant (Cody et al. 2000). This reaction has been suggested to proceed through the formation of iron carbonyl complexes and subsequent reduction of CO with H_2, which was produced through the oxidation of sulfide:

$$8)\ 2FeS + 6CO + 2RSH \rightleftharpoons Fe_2(RS)_2(CO)_6 + 2S^0 + H_2$$

$$9)\ 3CO + 2H_2 \rightleftharpoons C_3H_4O_3$$

Huber and Wächtershauser showed that CO can react with methane thiol to form the ‘activated’ thioester methyl-thioacetate (CH_3COSCH_3) (Huber and Wächtershäuser 1997), mimicking the biological process (for review, see (Bender et al. 2011)). They also showed that CO can form COS, which subsequently activates amino acids at the amine position, leading to their polymerization (Huber and Wächtershäuser 1998). It seems that hydrogenation of CO_2 with H_2 to form CO (which can equilibrate with formate (HCO_2^-) through hydration) could be a powerful harbinger of reactions relevant to early life, and these hydrogenations may have been performed by the first cells (Russell and Martin 2004; Ferry and House 2006).

C-C bond formation starting from CO_2 can be achieved with suitable catalysts and electron donors at modest temperatures and pressures. Metallic iron has been shown to facilitate the reduction of CO_2 to acetate with $E^{0`}$= -0.29V (Thauer 1977) vs. the standard hydrogen electrode (SHE) at pH 7 (He et al. 2010; Muchowska et al. 2017; Varma et al. 2018). But due to the lability of Fe^0 forming less reducing iron species in water, it is important to consider how electrons might continually reduce CO_2 with some specificity rather than simply reducing protons to H_2 and exhausting the reducing potential supplied.

Serpentinizing systems in some situations may provide a constant supply of H_2 and HS^- which form iron sulfide mineral phases reminiscent of tetragonal FeS cluster found in redox active enzymes (Mielke et al. 2010). A hint of the importance of these FeS clusters might be found in a synthetic analogue of the [2Fe2S] cofactor clusters found in contemporary biology, which has been shown to facilitate reductive carboxylations (**Figure 6)** (Nakajima et al. 1975). This reaction relies on sodium hydrosulfite as a reductant with $E^{'} \sim -0.66$V vs. SHE at pH 7 (Mayhew 1978) and was observed in solutions of tetrahydrofuran, methanol, and water. Possibly linking soluble carbon chemistry with insoluble minerals, metal sulfides have been shown to reduce CO_2 electrochemically (Yamaguchi et al. 2014; Kitadai et al. 2018). **Figure 1** depicts schematically the reduction of CO_2 to CH_4 in one electron reduction steps on a metal electrode. Depending on the electrode material, the reduction steps below CO can branch off into the production of methanol or C_2 compounds (Nie et al. 2013).

A very brief overview of hydrogenation in biology: energy and anabolism

Electron transfer reactions in the cell can be linked to respiratory processes, such as the hydrogenation of O_2 or sulfate to produce water or HS^-, respectively. In respiration, work is done as electrons move from a more negative potential to a more positive potential. In another mode of electron transfer that can involve hydrogenation reactions, an atom in a molecule can be reduced or oxidized as part of a biosynthetic pathway, that is, to form material used in constructing a cell. In this case, the primary purpose is not energy harvesting, but bio-molecular construction, and biologists refer to this as anabolism.

In the case of H_2, some organisms may oxidize it, and yet others may form it and release it. Whether H_2 is consumed or produced in a metabolism is related to the thermodynamic tendency (*i.e.* electrochemical potential) of molecules other than hydrogen to acquire electrons from H_2, or deliver them to protons. For example, if an organism is utilizing O_2 as an electron acceptor in the presence of H_2, there will be a tendency to pull electrons off of H_2 and combine them with O_2. Oxygen is such a powerful oxidant, that it "pulls" electrons from hydrogen even at non-measurable concentrations (Inskeep et al. 2005). To predict which direction electron transfer and hydrogenation reactions may occur it is useful to consider which molecules donate and accept electrons in and out of a given metabolism.

Many biological hydrogenations occur without the formation or consumption of H_2. These are transfer hydrogenations, since they involve the gain or loss of hydrogen but do not directly involve H_2 gas. For example, the ketone group of pyruvate can be reduced by two electrons to form the alcohol group of lactate (the reaction is illustrated in the center of Figure 1). The electron donor and hydrogenating agent in the reaction is the reduced form of the enzyme cofactor nicotinamide adenine dinucleotide (NADH), a biological two electron carrier (also

Box 2: Energy conservation in the Biological Cell 101

All life requires energy for maintenance and replication. Biologists commonly refer to the process of cellular energy harvesting as “conservation”. When they say this, they are not referring to the first law of thermodynamics! Energy conservation in biology refers to *conversion*; in the cell, it is about converting one form of energy to another. This conversion allows biology to temporarily capture energy, and divert it to cellular processes and functions. Biologists, consider “energy rich” molecules such as adenosine triphosphate (**ATP**), but the energy available from these molecules is directly related to their distance to equilibrium. In the case of ATP, the energy available is directly proportional to the concentrations of ATP and ADP, the hydrolysis substrate, and product in the cell. ATP hydrolysis can be coupled to another chemical reaction which would otherwise be unfavorable. Another form of “energy storage” or “energy harvesting” is by **chemiosmosis**, which involves coupling a chemical reaction to the movement of ions (often protons or sodium) across the membrane. Later, this offset in ion concentrations can be used to “push” a different reaction forward (for example, achieving a large offset in the concentration of ATP and ADP in the cell). In a classic and very valuable paper, Thauer et al. 1977 cited in the references outlined how chemical potentials could be connected to cell growth and physiology.

How is all this connected to hydrogenation? All known life couples electron transfer reactions to maintenance and replication (often through ATP as an intermediate). Since hydrogenation is one of the basic routes of moving electrons from one molecule to another, they are of basic importance to biology. In the cell, electron transfer reactions such as hydrogenation can be linked, our coupled to other reactions which allow the cell to conserve energy and propagate.

shown in Figure 1). This important electron carrier operates in biochemistry with the half cell reaction stoichiometry shown in Figure 3. Here the movement of the proton to and from NAD$^+$ (Nicotinamide Adenine Dinucleotide) occurs in the form of a hydride (H$^-$). Other electron carriers such as Flavin Adenine Dinucleotide (FAD) and the iron sulfur cluster containing protein ferredoxin operate in transfer hydrogenation reactions in the cell, and these molecules give cells a common electronic "currency".

In glycolysis, a central sugar metabolizing arm of metabolism, the intermediate glyceraldehyde 3-phosphate is oxidized and results in the formation of a phosphoester bond, which can be used subsequently to form ATP from ADP:

10) Glyceraldehyde-3Phosphate + NAD$^+$ + Phosphate $\rightleftharpoons$ 1-3Bis-phosphoglycerate + NADH

11) 1,3-Bisphosphoglycerate^{4-} + ADP^{3-} $\rightleftharpoons$ 3-Phosphoglycerate^{3-} + ATP^{4-}

This reaction is an example of how hydrogenation and dehydrogenation reactions being coupled to energy harvesting; an aldehyde is dehydrogenated, making possible the formation of a phosphoester compound. This latter compound can then go on and drive reactions such as ATP formation, and ATP is used broadly as a contributor of exergonic chemical potential in reactions.

In addition to sugars, organisms also synthesize amino acids and fatty acids through hydrogenations; in reverse, these molecules are oxidized by dehydrogenation. In addition to the water soluble hydrogenations noted above, an important class of fat soluble biomolecules, such as quinones and methanophenazine, allow for electron and proton entry (and exit) into biological lipid membranes, by acting as agents of trans hydrogenation (for example, see (Duszenko and Buan 2017). The ability to move charge into and across the membrane is one way that life accomplishes charge separation in chemiosmosis and temporarily captures energy for cellular processes, and again this example shows how critical hydrogenation reactions are in biological systems, which themselves are electronic. A basic schematic of one way biology uses these fat soluble transfer-hydrogenation reactions to build up a membrane spanning ion potential is shown in Figure 4. There, we can see a cartoon diagram of a cell membrane with two enzyme complexes embedded in the membrane. By having each enzyme catalyze a separate hydrogenation, and by sharing a common electronic intermediate (here drawn as "Q/QH_2", the cell is able to accomplish asymmetric charge movement across the membrane. This charge builds up, and is later on utilizable in the form of an energy storage system in a process called "chemiosmosis".

Case study: CO_2 hydrogenation to formate.

In biology, CO_2 is hydrogenated to formic acid HCOOH by several enzymes, including the enzyme hydrogen-dependent carbon dioxide reductase (HDCR) (Schuchmann and Müller 2013) and formate dehydrogenase (FDH) (Appel et al. 2013) (Figure 5). This reaction type of CO_2 hydrogenation is the first in the carbon metabolism of the globally important methanogens and acetogens (Thauer 1998; Thauer et al. 2008; Schuchmann and Müller 2014), although instead of catalyzing the production of formate, the biological enzymes catalyze the formation of carbon complexed on an organic scaffold which is sequentially reduced in the cell (for review, see (Maden 2000)). These methane- and acetate-forming organisms live in anoxic environments and couple the exergonic reduction (hydrogenation) of CO_2 to either methane or acetate to their growth. Interestingly, in reverse, acetate and methane can be used as metabolic fuel during anaerobic methane oxidation and anaerobic acetate oxidation depending on the availability of an electron acceptor of sufficient redox potential to make the net reactions favorable (Hattori 2008; Thauer 2011; McGlynn 2017).

Abiotic CO_2 reduction to formate and other reduced carbon species is of substantial interest for sustainable chemistry goals (Gurudayal et al. 2017; Wei et al. 2017), and has been investigated extensively by electrochemical means (Hori 2008). In addition to electrochemically driven reactions, CO_2 reduction to formate can take place at near ambient P/T conditions with synthetic organometallic cofactors (e.g. (Jószai and Joó 2007), or with natural minerals and metals at slightly higher T/P conditions (see **Methanation** section above).

Hydrogenations occurring in the atmosphere

Hydrogenation reactions in planetary atmospheres may have played an important role for the reduction of simple carbon species such as CO_2 and CO, and for CH_4 oxidation through dehydrogenation. In modern Earth's oxidizing atmosphere, hydrogenation of CO_2 and CO rarely occurs, and thus is not well understood. On the other hand, in reducing atmospheres, potentially like that of the early Earth and Mars, hydrogenation of CO_2 and CO could be initiated from UV photo-dissociation of H_2O and CO_2:

$$12)\ H_2O + h\nu \rightarrow H + OH$$

$$13)\ CO_2 + h\nu \rightarrow CO + O$$

where $h\nu$ represents < 200 nm ultraviolet light. The back reaction of R13 is very slow, and thus the oxidation of CO largely proceeds through the reaction with OH radical:

$$14)\ CO + OH \rightarrow CO_2 + H$$

However, when the atmosphere is reducing, hydrogenation of CO could form formyl radical (HCO) and then formaldehyde (HCHO), mainly through the following reaction (Pinto et al. 1980):

$$15)\ CO + H + M \rightarrow HCO + M$$

16) $HCO + HCO \rightarrow HCHO + CO$

where M represents any third-body reaction partner.

Once the HCO and HCHO are formed, number of successive radical chain reactions can occur. Several laboratory experiments have demonstrated that not only formaldehyde, but also acetaldehyde, methanol, and carboxylic acids are synthesized by UV irradiation of CO-bearing atmosphere under the presence of water vapor (Bar-Nun and Chang 1983; Kawade 2018). The reaction pathways to produce these compounds from HCHO is largely uncertain, though possibly proceed through the following reactions:

17) $HCHO + OH \rightarrow H_2O + HCO$

18) $HCHO + OH \rightarrow HCOOH + H$

19) $HCHO + H \rightarrow H_2 + HCO$

20) $HCHO + H + M \rightarrow CH_3O + M$

21) $CH_3O + H_2 \rightarrow CH_3OH + H$

These studies suggest that the abiotic synthesis of simple organic compounds is possible particularly when the H/OH ratio is high (i.e. reducing atmosphere), because hydrogenation of CO (R15) is faster than the oxidation of CO (R14). Therefore, the production rate of these organics largely depends on total redox state of the atmosphere.

On early Earth and Mars, the most abundant and efficient reducing agent may have been H_2 and possibly CH_4, which can scavenge excess OH and thus buffer the reducing atmosphere. In an H_2-rich and/or CH_4-rich atmosphere, however, hydrogen escape into space is more efficient than oxidizing atmosphere. This is because H_2 and CH_4 are efficient carriers of hydrogen to the top of the atmosphere, whereas H_2O is not owing to condensation in the mid part of the atmosphere. Consequently, escape rate of hydrogen is high in a reducing atmosphere, which results in faster oxidation of the atmosphere in a geological time scale.

Implications

Abiotic reactions and reactions pathways involving hydrogenation/dehydrogenation can be challenging to identify owing to the abundance of oxygen in geological fluids in the upper mantle, crust, and atmosphere. Several reactions mentioned in this article are rarely observed in natural settings as written, and represent simplifications and/or intermediates of more complex aqueous solutions and reaction pathways. Exceptions may exist in settings where reducing conditions can be achieved and maintained over significant time scales. In the lithosphere, hydrothermal alteration of ultramafic rocks, or serpentinization, is certainly among the best candidates, even though our understanding of these systems is still largely incomplete and may incorporate other H_2 generating processes such as radiolytic and mechanochemical splitting of water. Hydrogenation reactions in the deep Earth, such as in the mantle, may be more common owing to the decrease in oxygen fugacity with depth. Great effort is still demanded in order to understand hydrogenation/dehydrogenation processes and their role over the Earth's history. The potential outcomes of future research span critical features of science and the modern society, such as global climate changes and the emergence/sustainability of life on our planet and beyond (Gurudayal et al. 2017). Experimental and theoretical studies, and their application to past and present natural settings have made great steps forward over the last decades, and fully justify additional effort in the future.

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References cited list

Allen, D.E., and Seyfried, W.E. (2003) Compositional controls on vent fluids from ultramafic-hosted hydrothermal systems at mid-ocean ridges: An experimental study at 400°C, 500 bars. Geochimica et Cosmochimica Acta, 67, 1531–1542.

Allen, D.E., and Seyfried, W.E. (2003) Compositional controls on vent fluids from ultramafic-hosted hydrothermal systems at mid-ocean ridges: An experimental study at 400°C, 500 bars. Geochimica et Cosmochimica Acta, 67, 1531–1542.

Anderson, R.B. (1978) Schulz-Flory equation. Journal of Catalysis, 55, 114–115.

Appel, A.M., Bercaw, J.E., Bocarsly, A.B., Dobbek, H., DuBois, D.L., Dupuis, M., Ferry, J.G., Fujita, E., Hille, R., Kenis, P.J.A., and others (2013) Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO2 Fixation. Chemical Reviews, 113, 6621–6658.

Baldauf-Sommerbauer, G., Lux, S., Aniser, W., and Siebenhofer, M. (2016) Reductive Calcination of Mineral Magnesite: Hydrogenation of Carbon Dioxide without Catalysts. Chemical Engineering & Technology, 39, 2035–2041.

Bali, E., Audétat, A., and Keppler, H. (2013) Water and hydrogen are immiscible in Earth's mantle. Nature, 495, 220–222.

Bar-Nun, A., and Chang, S. (1983) Photochemical reactions of water and carbon monoxide in Earth's primitive atmosphere. Journal of Geophysical Research: Oceans, 88, 6662–6672.

Barton, L.L., Ed. (1995) Sulfate-Reducing Bacteria, 1st ed., 352 p. Springer.

Barton, L.L., and Fauque, G.D. (2009) Biochemistry, physiology and biotechnology of sulfate-reducing bacteria. Advances in Applied Microbiology, 68, 41–98.

Beller, M., and Bornscheuer, U.T. (2014) CO2 Fixation through Hydrogenation by Chemical or Enzymatic Methods. Angewandte Chemie International Edition, 53, 4527–4528.

Bender, G., Pierce, E., Hill, J.A., Darty, J.E., and Ragsdale, S.W. (2011) Metal centers in the anaerobic microbial metabolism of CO and CO2. Metallomics: Integrated Biometal Science, 3, 797–815.

Brandes, J.A., Boctor, N.Z., Cody, G.D., Cooper, B.A., Hazen, R.M., and Yoder, H.S. (1998) Abiotic nitrogen reduction on the early Earth. Nature, 395, 365–367.

Bulen, W.A., and LeComte, J.R. (1966) The nitrogenase system from Azotobacter: two-enzyme requirement for N2 reduction, ATP-dependent H2 evolution, and ATP hydrolysis. Proceedings of the National Academy of Sciences of the United States of America, 56, 979–986.

Cadle, R.D. (1980) A comparison of volcanic with other fluxes of atmospheric trace gas constituents. Reviews of Geophysics, 18, 746–752.

Charlou, J.L., Donval, J.P., Fouquet, Y., Jean-Baptiste, P., and Holm, N. (2002) Geochemistry of high H2 and CH4 vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14′N, MAR). Chemical Geology, 191, 345–359.

Cody, G.D., Boctor, N.Z., Filley, T.R., Hazen, R.M., Scott, J.H., Sharma, A., and Yoder, H.S. (2000) Primordial Carbonylated Iron-Sulfur Compounds and the Synthesis of Pyruvate. Science, 289, 1337–1340.

Connolly, J.A.D. (1995) Phase diagram methods for graphitic rocks and application to the system C−O−H−FeO−TiO2−SiO2. Contributions to Mineralogy and Petrology, 119, 94–116.

Deines, P. (1980) The isotropic composition of reduced organic carbon. In P. Fritz and J. Fontes, Eds., Handbook of Environmental Isotope Geology Vol. 1, pp. 329–406. Elsevier.

Diender, M., Stams, A.J.M., and Sousa, D.Z. (2015) Pathways and Bioenergetics of Anaerobic Carbon Monoxide Fermentation. Frontiers in Microbiology, 6.

Duszenko, N., and Buan, N.R. (2017) Physiological Evidence for Isopotential Tunneling in the Electron Transport Chain of Methane-Producing Archaea. Applied and Environmental Microbiology, 83.

Egorov, A., M., Avilova, T., V., Dikov, M., M., Popov, V., O., Rodionov, Y., V., and Berezin, I., V. (1979) NAD‐Dependent Formate Dehydrogenase from Methylotrophic Bacterium, Strain. European Journal of Biochemistry, 99, 569–576.

Escario, S., Godard, M., Gouze, P., and Leprovost, R. (2018) Experimental study of the effects of solute transport on reaction paths during incipient serpentinization. Lithos, 323, 191–207.

Etiope, G., and Sherwood Lollar, B. (2013) ABIOTIC METHANE ON EARTH.

Ferry, J.G. (1990) Formate dehydrogenase. FEMS Microbiology Reviews, 7, 377–382.

Ferry, J.G., and House, C.H. (2006) The stepwise evolution of early life driven by energy conservation. Molecular Biology and Evolution, 23, 1286–1292.

Gadalla, A.M., and Bower, B. (1988) The role of catalyst support on the activity of nickel for reforming methane with CO2. Chemical Engineering Science, 43, 3049–3062.

Giardini, A.A., and Salotti, C.A. (1969) Kinetics and relations in the calcite-hydrogen reaction and relations in the dolomite-hy-drogen and siderite-hydrogen systems. American Mineralogist, 54, 1151–1172.

Goethel, P.J., and Yang, R.T. (1988) Mechanism of graphite hydrogenation catalyzed by ruthenium particles. Journal of Catalysis, 111, 220–226.

Goldstein, T.P., and Aizenshtat, Z. (1994) Thermochemical sulfate reduction a review. Journal of Thermal Analysis, 42, 241–290.

Griffin, W.L., Huang, J.-X., Thomassot, E., Gain, S.E.M., Toledo, V., and O'Reilly, S.Y. (2018) Super-reducing conditions in ancient and modern volcanic systems: sources and behaviour of carbon-rich fluids in the lithospheric mantle. Mineralogy and Petrology.

Gurudayal, Bullock, J., F. Srankó, D., M. Towle, C., Lum, Y., Hettick, M., C. Scott, M., Javey, A., and Ager, J. (2017) Efficient solar-driven electrochemical CO 2 reduction to hydrocarbons and oxygenates. Energy & Environmental Science, 10, 2222–2230.

Hattori, S. (2008) Syntrophic acetate-oxidizing microbes in methanogenic environments. Microbes and Environments, 23, 118–127.

He, C., Tian, G., Liu, Z., and Feng, S. (2010) A Mild Hydrothermal Route to Fix Carbon Dioxide to Simple Carboxylic Acids. Organic Letters, 12, 649–651.

Hoehler, T.M., Alperin, M.J., Albert, D.B., and Martens, C.S. (1994) Field and laboratory studies of methane oxidation in an anoxic marine sediment: Evidence for a methanogen-sulfate reducer consortium. Global Biogeochemical Cycles, 8, PP. 451-463.

Hori, Y. (2008) Electrochemical CO2 Reduction on Metal Electrodes. In C.G. Vayenas, R.E. White, and M.E. Gamboa-Aldeco, Eds., Modern Aspects of Electrochemistry pp. 89–189. Springer New York, New York, NY.

Horita, J., and Berndt, M.E. (1999) Abiogenic Methane Formation and Isotopic Fractionation Under Hydrothermal Conditions. Science, 285, 1055–1057.

Huber, C., and Wächtershäuser, G. (1997) Activated Acetic Acid by Carbon Fixation on (Fe,Ni)S Under Primordial Conditions. Science, 276, 245–247.

Huber, C., and Wächtershäuser, G. (1998) Peptides by Activation of Amino Acids with CO on (Ni,Fe)S Surfaces: Implications for the Origin of Life. Science, 281, 670–672.

Inskeep, W.P., Ackerman, G.G., Taylor, W.P., Kozubal, M., Korf, S., and Macur, R.E. (2005) On the energetics of chemolithotrophy in nonequilibrium systems: case studies of geothermal springs in Yellowstone National Park. Geobiology, 3, 297–317.

Jószai, I., and Joó, F. (2007) Hydrogenation of calcium carbonate in aqueous systems catalyzed by Rh(I)- and Ru(II)-complexes using poly(methylhydrosiloxane) or hypophosphite as hydrogen sources. Reaction Kinetics and Catalysis Letters, 91, 361–368.

Kawade, W. (2018) Experimental study on UV synthesis of organic compounds from CO and CO2 atmosphere. Tokyo Institute of Technology.

Kawasumi, T., Igarashi, Y., Kodama, T., and Minoda, Y. (1980) Isolation of Strictly Thermophilic and Obligately Autotrophic Hydrogen Bacteria. Agricultural and Biological Chemistry, 44, 1985–1986.

Kitadai, N., Nakamura, R., Yamamoto, M., Takai, K., Li, Y., Yamaguchi, A., Gilbert, A., Ueno, Y., Yoshida, N., and Oono, Y. (2018) Geoelectrochemical CO production: Implications for the autotrophic origin of life. Science Advances, 4, eaao7265.

Klein, F., and Bach, W. (2009) Fe–Ni–Co–O–S Phase Relations in Peridotite–Seawater Interactions. Journal of Petrology, 50, 37–59.

Klein, F., Bach, W., and McCollom, T.M. (2013) Compositional controls on hydrogen generation during serpentinization of ultramafic rocks. Lithos, 178, 55–69.

Klein, F., Grozeva, N.G., Seewald, J.S., McCollom, T.M., Humphris, S.E., Moskowitz, B., Berquó, T.S., and Kahl, W.-A. (2015) Experimental constraints on fluid-rock reactions during incipient serpentinization of harzburgite. American Mineralogist, 100, 991–1002.

Klein, F., Grozeva, N.G., and Seewald, J.S. (2019) Abiotic methane synthesis and serpentinization in olivine-hosted fluid inclusions. Proceedings of the National Academy of Sciences, 116, 17666–17672.

Lai, G.Y. (2007) High-temperature Corrosion and Materials Applications, 461 p. ASM International.

Lamadrid, H.M., Rimstidt, J.D., Schwarzenbach, E.M., Klein, F., Ulrich, S., Dolocan, A., and Bodnar, R.J. (2017) Effect of water activity on rates of serpentinization of olivine. Nature Communications, 8, 16107.

Lang, S.Q., Früh-Green, G.L., Bernasconi, S.M., Lilley, M.D., Proskurowski, G., Méhay, S., and Butterfield, D.A. (2012) Microbial utilization of abiogenic carbon and hydrogen in a serpentinite-hosted system. Geochimica et Cosmochimica Acta, 92, 82–99.

Lang, S.Q., Früh-Green, G.L., Bernasconi, S.M., Brazelton, W.J., Schrenk, M.O., and McGonigle, J.M. (2018) Deeply-sourced formate fuels sulfate reducers but not methanogens at Lost City hydrothermal field. Scientific Reports, 8, 1–10.

Lazar, C., Zhang, C., Manning, C.E., and Mysen, B.O. (2014) Redox effects on calcite-portlandite-fluid equilibria at forearc conditions: Carbon mobility, methanogenesis, and reduction melting of calcite. American Mineralogist, 99, 1604–1615.

Lux, S., Baldauf‐Sommerbauer, G., and Siebenhofer, M. (2018) Hydrogenation of Inorganic Metal Carbonates: A Review on Its Potential for Carbon Dioxide Utilization and Emission Reduction. ChemSusChem, 11, 3357–3375.

Maden, B.E. (2000) Tetrahydrofolate and tetrahydromethanopterin compared: functionally distinct carriers in C1 metabolism. The Biochemical Journal, 350 Pt 3, 609–629.

Maia, L.B., Moura, I., and Moura, J.J.G. (2017) Molybdenum and tungsten-containing formate dehydrogenases: Aiming to inspire a catalyst for carbon dioxide utilization. Inorganica Chimica Acta, 455, 350–363.

Malvoisin, B., and Brunet, F. (2014) Water diffusion-transport in a synthetic dunite: Consequences for oceanic peridotite serpentinization. Earth and Planetary Science Letters, 403, 263–272.

Martin, B., and Fyfe, W.S. (1970) Some experimental and theoretical observations on the kinetics of hydration reactions with particular reference to serpentinization. Chemical Geology, 6, 185–202.

Mayhew, S.G. (1978) The Redox Potential of Dithionite and SO−2 from Equilibrium Reactions with Flavodoxins, Methyl Viologen and Hydrogen plus Hydrogenase. European Journal of Biochemistry, 85, 535–547.

McCollom, T.M. (2003) Formation of meteorite hydrocarbons from thermal decomposition of siderite (FeCO3). Geochimica et Cosmochimica Acta, 67, 311–317.

McCollom, T.M. (2016) Abiotic methane formation during experimental serpentinization of olivine. Proceedings of the National Academy of Sciences, 113, 13965–13970.

McCollom, T.M., and Bach, W. (2009) Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. Geochimica et Cosmochimica Acta, 73, 856–875.

McDermott, J.M., Seewald, J.S., German, C.R., and Sylva, S.P. (2015) Pathways for abiotic organic synthesis at submarine hydrothermal fields. Proceedings of the National Academy of Sciences, 112, 7668–7672.

McGlynn, S.E. (2017) Energy Metabolism during Anaerobic Methane Oxidation in ANME Archaea. Microbes and Environments, 32, 5–13.

Miao, B., Ma, S.S.K., Wang, X., Su, H., and Chan, S.H. (2016) Catalysis mechanisms of CO2 and CO methanation. Catalysis Science & Technology, 6, 4048–4058.

Mielke, R.E., Russell, M.J., Wilson, P.R., McGlynn, S.E., Coleman, M., Kidd, R., and Kanik, I. (2010) Design, Fabrication, and Test of a Hydrothermal Reactor for Origin-of-Life Experiments. Astrobiology, 10, 799–810.

Muchowska, K.B., Varma, S.J., Chevallot-Beroux, E., Lethuillier-Karl, L., Li, G., and Moran, J. (2017) Metals promote sequences of the reverse Krebs cycle. Nature Ecology & Evolution, 1, 1716.

Nakajima, T., Yabushita, Y., and Tabushi, I. (1975) Amino acid synthesis through biogenetic-type CO2 fixation. Nature, 256, 60–61.

Nie, X., Esopi, M.R., Janik, M.J., and Asthagiri, A. (2013) Selectivity of CO(2) reduction on copper electrodes: the role of the kinetics of elementary steps. Angewandte Chemie (International Ed. in English), 52, 2459–2462.

Nitschke, W., and Russell, M.J. (2009) Hydrothermal focusing of chemical and chemiosmotic energy, supported by delivery of catalytic Fe, Ni, Mo/W, Co, S and Se, forced life to emerge. Journal of Molecular Evolution, 69, 481–496.

Padeste, C., Oswald, H.R., and Reller, A. (1991) The thermal behaviour of pure and nickel-doped hydromagnesite in different atmospheres. Materials Research Bulletin, 26, 1263–1268.

Perry, E.C., and Ahmad, S.N. (1977) Carbon isotope composition of graphite and carbonate minerals from 3.8-AE metamorphosed sediments, Isukasia, Greenland. Earth and Planetary Science Letters, 36, 280–284.

Pinto, J.P., Gladstone, G.R., and Yung, Y.L. (1980) Photochemical Production of Formaldehyde in Earth's Primitive Atmosphere. Science, 210, 183–185.

Popov, V.O., and Lamzin, V.S. (1994) NAD(+)-dependent formate dehydrogenase. Biochemical Journal, 301, 625–643.

Preiner, M., Xavier, J.C., Sousa, F.L., Zimorski, V., Neubeck, A., Lang, S.Q., Greenwell, H.C., Kleinermanns, K., Tüysüz, H., McCollom, T.M., and others (2018) Serpentinization: Connecting Geochemistry, Ancient Metabolism and Industrial Hydrogenation. Life (Basel, Switzerland), 8.

Proskurowski, G., Lilley, M.D., Seewald, J.S., Früh-Green, G.L., Olson, E.J., Lupton, J.E., Sylva, S.P., and Kelley, D.S. (2008) Abiogenic hydrocarbon production at lost city hydrothermal field. Science (New York, N.Y.), 319, 604–607.

Reller, A., Emmenegger, R., Padeste, C., and Oswald, H.-R. (1991, September) Thermochemical Reactivity of Metal Carbonates. Text.

Rönsch, S., Schneider, J., Matthischke, S., Schlüter, M., Götz, M., Lefebvre, J., Prabhakaran, P., and Bajohr, S. (2016) Review on methanation – From fundamentals to current projects. Fuel, 166, 276–296.

Rumble, D., and Hoering, T.C. (1986) Carbon isotope geochemistry of graphite vein deposits from New Hampshire, U.S.A. Geochimica et Cosmochimica Acta, 50, 1239–1247.

Russell, M.J., and Martin, W. (2004) The rocky roots of the acetyl-CoA pathway. Trends in Biochemical Sciences, 29, 358–363.

Sabatier, P., and Senderens, J. (1902) New synthesis of methane. Compt Rend, 134, 514–516.

Salotti, C.A., Heinrich, E.W., and Giardini, A.A. (1971) Abiotic carbon and the formation of graphite deposits. Economic Geology, 66, 929–932.

Schoepp-Cothenet, B., van Lis, R., Philippot, P., Magalon, A., Russell, M.J., and Nitschke, W. (2012) The ineluctable requirement for the trans-iron elements molybdenum and/or tungsten in the origin of life. Scientific Reports, 2.

Schoonen, M.A.A., and Xu, Y. (2001) Nitrogen Reduction Under Hydrothermal Vent Conditions: Implications for the Prebiotic Synthesis of C-H-O-N Compounds. Astrobiology, 1, 133–142.

Schuchmann, K., and Müller, V. (2013) Direct and Reversible Hydrogenation of CO2 to Formate by a Bacterial Carbon Dioxide Reductase. Science, 342, 1382–1385.

Schuchmann, K., and Müller, V. (2014) Autotrophy at the thermodynamic limit of life: a model for energy conservation in acetogenic bacteria. Nature Reviews. Microbiology, 12, 809–821.

Seewald, J.S., Zolotov, M.Yu., and McCollom, T. (2006) Experimental investigation of single carbon compounds under hydrothermal conditions. Geochimica et Cosmochimica Acta, 70, 446–460.

Simon, J., van Spanning, R.J.M., and Richardson, D.J. (2008) The organisation of proton motive and non-proton motive redox loops in prokaryotic respiratory systems. Biochimica Et Biophysica Acta, 1777, 1480–1490.

Smirnov, A., Hausner, D., Laffers, R., Strongin, D.R., and Schoonen, M.A. (2008) Abiotic ammonium formation in the presence of Ni-Fe metals and alloys and its implications for the Hadean nitrogen cycle. Geochemical Transactions, 9, 5.

Smit, K.V., Shirey, S.B., Stern, R.A., Steele, A., and Wang, W. (2016) Diamond growth from C–H–N–O recycled fluids in the lithosphere: Evidence from CH4 micro-inclusions and δ13C–δ15N–N content in Marange mixed-habit diamonds. Lithos, C, 68–81.

Spear, J.R., Walker, J.J., McCollom, T.M., and Pace, N.R. (2005) Hydrogen and bioenergetics in the Yellowstone geothermal ecosystem. Proceedings of the National Academy of Sciences, 102, 2555–2560.

Syverson, D.D., Tutolo, B.M., Borrok, D.M., and Seyfried, W.E. (2017) Serpentinization of olivine at 300°C and 500bars: An experimental study examining the role of silica on the reaction path and oxidation state of iron. Chemical Geology, 475, 122–134.

Tao, R., Zhang, L., Tian, M., Zhu, J., Liu, X., Liu, J., Höfer, H.E., Stagno, V., and Fei, Y. (2018) Formation of abiotic hydrocarbon from reduction of carbonate in subduction zones: Constraints from petrological observation and experimental simulation. Geochimica et Cosmochimica Acta, 239, 390–408.

Thauer, R.K. (1998) Biochemistry of methanogenesis: a tribute to Marjory Stephenson. 1998 Marjory Stephenson Prize Lecture. Microbiology (Reading, England), 144 (Pt 9), 2377–2406.

Thauer, R.K. (2010) Functionalization of methane in anaerobic microorganisms. Angewandte Chemie (International ed. in English), 49, 6712–6713.

Thauer, R.K. (2011) Anaerobic oxidation of methane with sulfate: on the reversibility of the reactions that are catalyzed by enzymes also involved in methanogenesis from CO2. Current Opinion in Microbiology, 14, 292–299.

Thauer, R.K., Jungermann, K., and Decker, K. (1977) Energy conservation in chemotrophic anaerobic bacteria. Bacteriological Reviews, 41, 100–180.

Thauer, R.K., Kaster, A.-K., Seedorf, H., Buckel, W., and Hedderich, R. (2008) Methanogenic archaea: ecologically relevant differences in energy conservation. Nature Reviews. Microbiology, 6, 579–591.

Thomassot, E., Cartigny, P., Harris, J.W., and (Fanus) Viljoen, K.S. (2007) Methane-related diamond crystallization in the Earth's mantle: Stable isotope evidences from a single diamond-bearing xenolith. Earth and Planetary Science Letters, 257, 362–371.

Tsuneto, A., Kudo, A., Saito, N., and Sakata, T. (1992) Hydrogenation of Solid State Carbonates. Chemistry Letters, 21, 831–834.

Varma, S.J., Muchowska, K.B., Chatelain, P., and Moran, J. (2018) Native iron reduces CO 2 to intermediates and end-products of the acetyl-CoA pathway. Nature Ecology & Evolution, 2, 1019.

Vitale Brovarone, A., Martinez, I., Elmaleh, A., Compagnoni, R., Chaduteau, C., Ferraris, C., and Esteve, I. (2017) Massive production of abiotic methane during subduction evidenced in metamorphosed ophicarbonates from the Italian Alps. Nature Communications, 8, 14134.

Wang, D.T., Reeves, E.P., McDermott, J.M., Seewald, J.S., and Ono, S. (2018) Clumped isotopologue constraints on the origin of methane at seafloor hot springs. Geochimica et Cosmochimica Acta, 223, 141–158.

Wei, J., Ge, Q., Yao, R., Wen, Z., Fang, C., Guo, L., Xu, H., and Sun, J. (2017) Directly converting CO2 into a gasoline fuel. Nature Communications, 8, 15174.

Welhan, J.A. (1988) Origins of methane in hydrothermal systems. Chemical Geology, 71, 183–198.

Yamaguchi, A., Yamamoto, M., Takai, K., Ishii, T., Hashimoto, K., and Nakamura, R. (2014) Electrochemical CO2 Reduction by Ni-containing Iron Sulfides: How Is CO2 Electrochemically Reduced at Bisulfide-Bearing Deep-sea Hydrothermal Precipitates? Electrochimica Acta, 141, 311–318.

Yoshida, N., Hattori, T., Komai, E., and Wada, T. (1999) Methane formation by metal-catalyzed hydrogenation of solid calcium carbonate. Catalysis Letters, 58, 119–122.

Table

Some hydrogenation/dehydrogenation reactions of biogeochemical importance involving Carbon, Nitrogen, and Sulfur

Reaction	Abiotic path	references	Biotic path	references
$N_2 + 6e^- + 6H^+ = 2NH_3$	Lightning, Some reduced minerals	(Brandes et al. 1998; Schoonen and Xu 2001; Smirnov et al. 2008)	Nitrogenase	(Bulen and LeComte 1966)
$CO_2 + 8e^- + 8H^+ = CH_4 + 2H_2O$	Carbonate methanation	(Giardini and Salotti 1969; Reller et al. 1991; Yoshida et al. 1999)	methanogenesis/methane oxidation	(Hoehler et al. 1994; Thauer et al. 2008; Thauer 2010)
$CO_2 + 2e^- + 2H^+ = HCOOH$	Reduced minerals	e.g. (Beller and Bornscheuer 2014)	Formate dehydrogenase	(Ferry 1990; Maia et al. 2017)
$SO_4^{-2} + 8e^- + 9H^+ = HS^- + 4H_2O$	High temperature , reduced minerals	(Goldstein and Aizenshtat 1994)	Sulfate reduction	(Barton 1995; Barton and Fauque 2009)
$O_2 + 2H_2 = 2H_2O$			Microbial lithotrophy	(Kawasumi et al. 1980; Spear et al. 2005)

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Figure 1. A broad overview of hydrogenation reactions of carbon discussed in the text. CO_2 reduction pathways encountered in methanogenesis and electroreduction on metal surfaces are shown on the right and left. Only the two electron reduction steps in the biological methanogenesis pathway are pictured on the right, including methanofuran (MFR) with a bound formyl-moeity and various states carbon bound to the cofactor tetrahydromethanopterin (H_4MPT) are shown. For more detail of the enzymology, the reader is guided to excelent reviews (Thauer 1998; Thauer et al. 2008). On the left, one example of an electrochemical carbon reduction pathway is shown, in this case the reduction arrow steps are one electron reduction steps, which can diverge in their composition depending on the metal surfaces and the final products e.g. ethylene or methanol (Nie et al. 2013). In the center, some typical hydrogenation reactions encountered in organisms and abiotically propagate from pyruvate. From left to right below pyruvate are pictured the reduction of alkenes, the reduction of NAD, and the reductive amination of pyruvate to the amino acid alanine.

Figure 2. Two mechanisms for abiotic methanation. Top: associative pathway, whereby C-O bond breaking is assisted by addition of H_{ad}. Bottom: dissociative pathway, whereby the C-O bond is directly dissociated on the catalyst surface. Modified from (Miao et al. 2016).

Figure 3: An example of biological transfer hydrogenation: nicotinamide adenine dinucleotide (NADH) can be reversibly oxidized and reduced, here shown as NAD^+ on the left, and NADH on the right.

Figure 4: A “redox loop” mechanism coupling hydrogenation reactions to chemiosmosis in biology. Hydrogenation of Quinol (Q) inside the cell membrane (grey) by H_2, and subsequent trans-hydrogenation of an intracellular electron acceptor (R), leads to charge separation across a biological membrane and the buildup of a chemiosmotic potential. Negative charge (electrons) goes in, positive charge (protons) go out. Variations on this theme are observed in biology, this figure represents one example as a starting point for deeper inquiry. The interested reader is directed to an excellent review (Simon et al. 2008).

Figure 5: Examples of enzymes and the hydrogenation chemistry they catalyze with CO_2 a) Metal-independent formate dehydrogenase (FDH) catalyzes reversible formate dehydration to CO_2 via a transfer hydrogenation of the biological electron carrier $NAD(P)^+$ (Egorov et al. 1979; Popov and Lamzin 1994). b) The hydrogen dependent carbon dioxide reductase (HDCR) is a protein complex consisting of hydrogenase (Hyd) and formate dehydrogenase (FDH) subunits that together catalyzes CO_2 reduction to formate with electrons from H_2 (e.g. in *Acetobacterium woodii*; (Schuchmann and Müller 2013)). c) The FDH subunit of HDCR can also reduce CO_2 through oxidation of CO to CO_2 ($E^{0'}$= -520mV; (Schuchmann and Müller 2013; Diender et al. 2015) via the carbon monoxide dehydrogenase (CODH). Except the metal free FDH, all these enzymes have in common a reliance on transition metal ions including Mo, W, Fe, and Ni, for catalysis (Schoepp-Cothenet et al. 2012; Schuchmann and Müller 2013; Maia et al. 2017).

Figure 6: Reductive carboxylation of carboxylic acids as investigated by Nakajima et al. The reaction took place in a CO_2 saturated mixture of tetrahydrofuran, methanol and water (4:2:1)

with sodium hydrosulfite as the reductant. [2Fe-2S] represents a two iron, two iron cluster, which is presumed catalyst of the reaction.

Figures

Figure 1

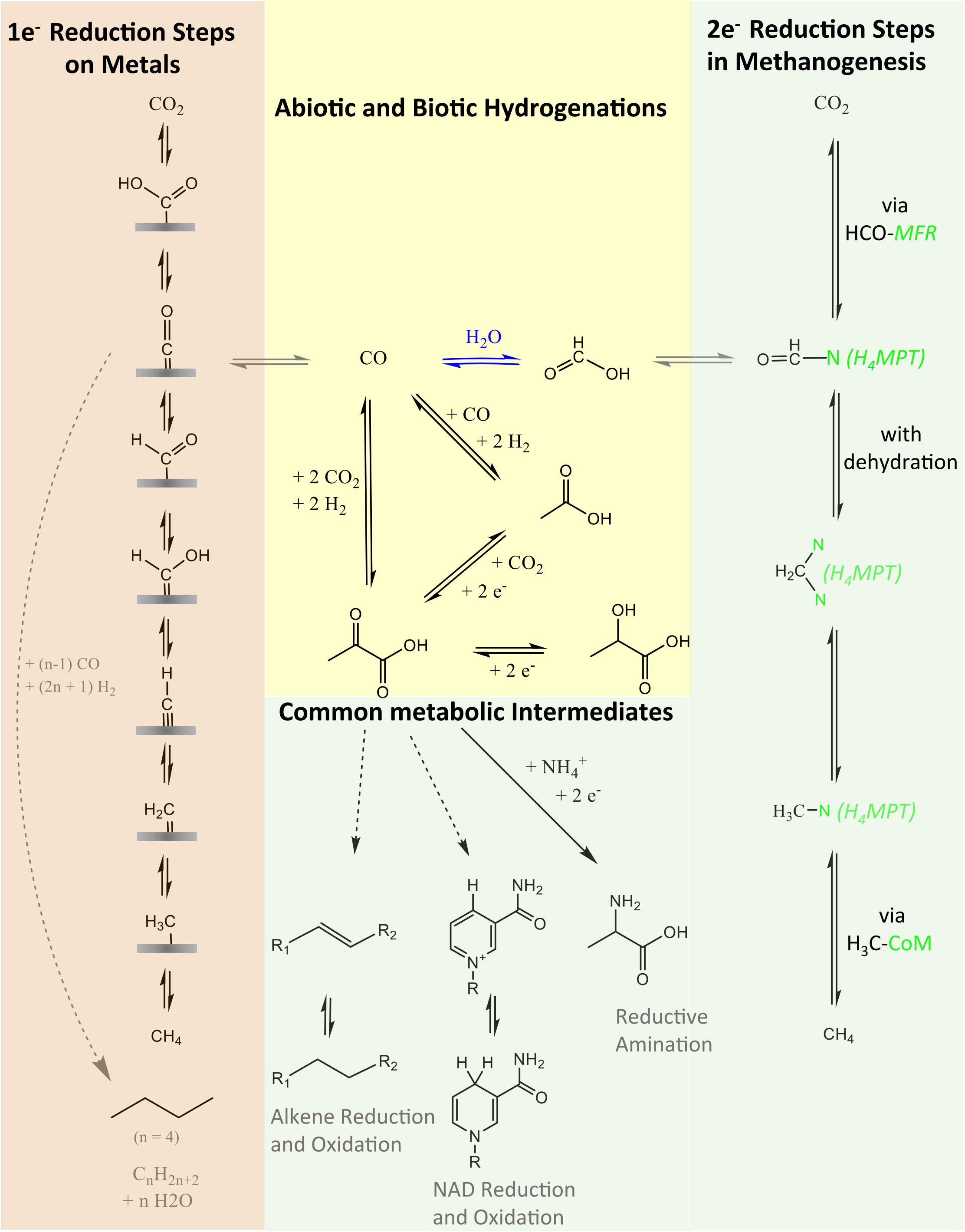

1e- Reduction Steps on Metals
Abiotic and Biotic Hydrogenations
2e- Reduction Steps in Methanogenesis
CO2
HO C O
O C
H C O
H C OH
H C
H2C
H3C
CH4
+ (n-1) CO
+ (2n + 1) H2
(n = 4)
CnH2n+2
+ n H2O
CO
H2O
+ CO
+ 2 H2
+ 2 CO2
+ 2 H2
+ CO2
+ 2 e-
+ 2 e-
OH
O
Common metabolic Intermediates
+ NH4+
+ 2 e-
R1
R2
Alkene Reduction and Oxidation
H NH2
N+
R
H H NH2
NAD Reduction and Oxidation
NH2
OH
Reductive Amination
CO2
via
HCO-MFR
O=C—N (H4MPT)
with dehydration
H2C (H4MPT)
N
H3C−N (H4MPT)
via
H3C-CoM
CH4

Figure 2

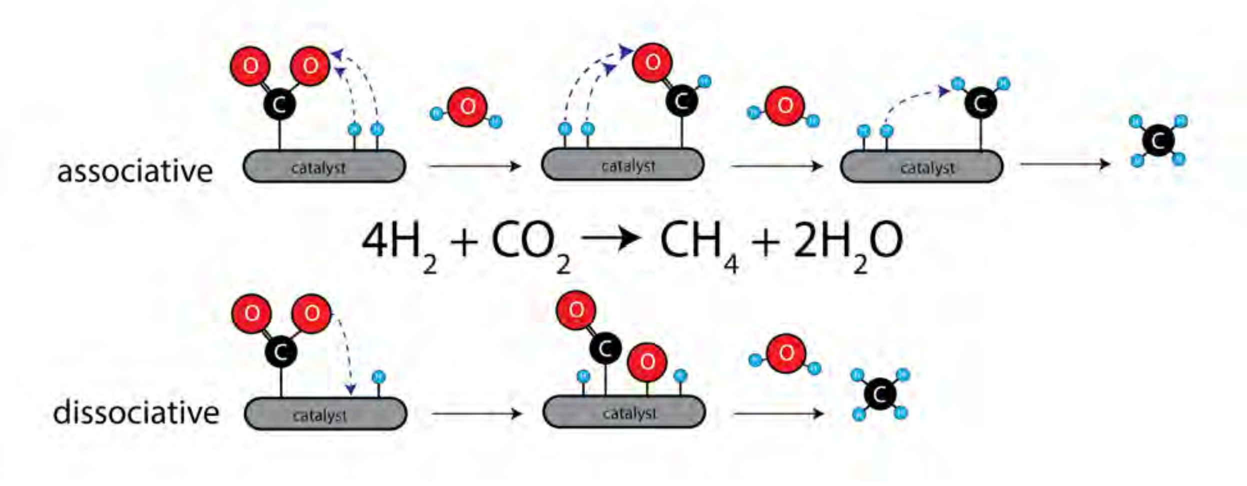
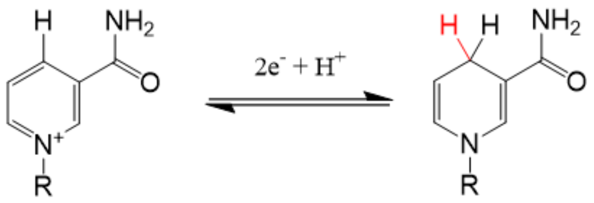


Figure 3



$E^{0'}$ = -320mV vs. SHE, pH 7

Figure 4

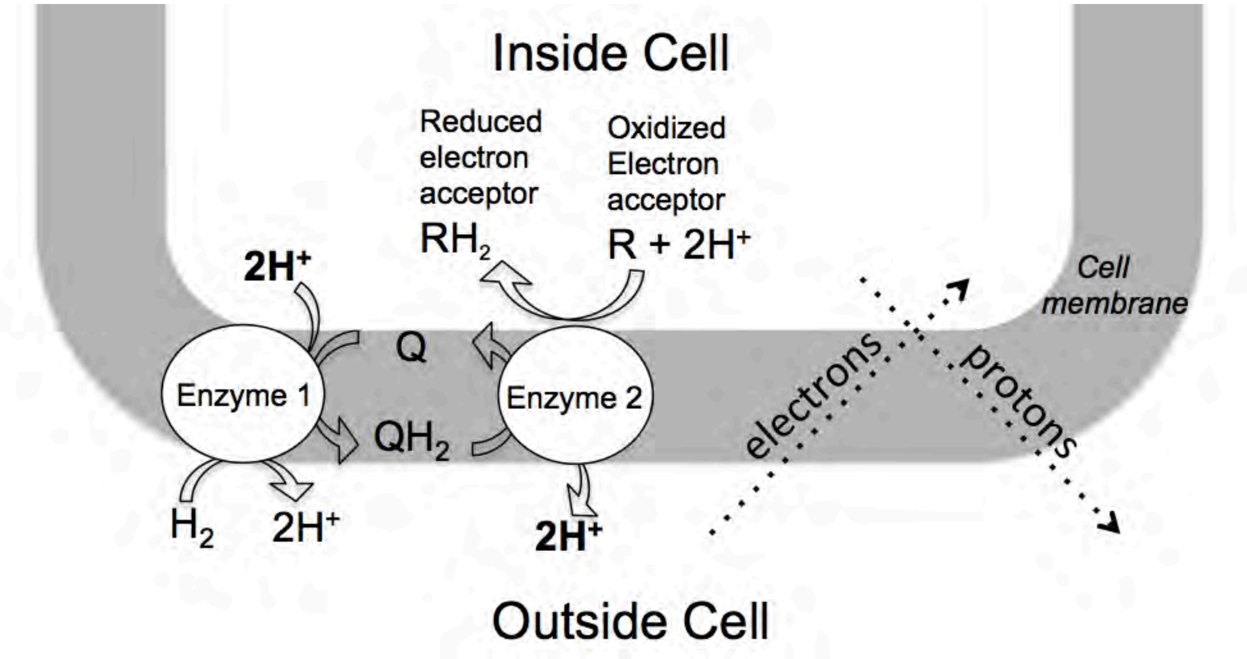


Figure 5

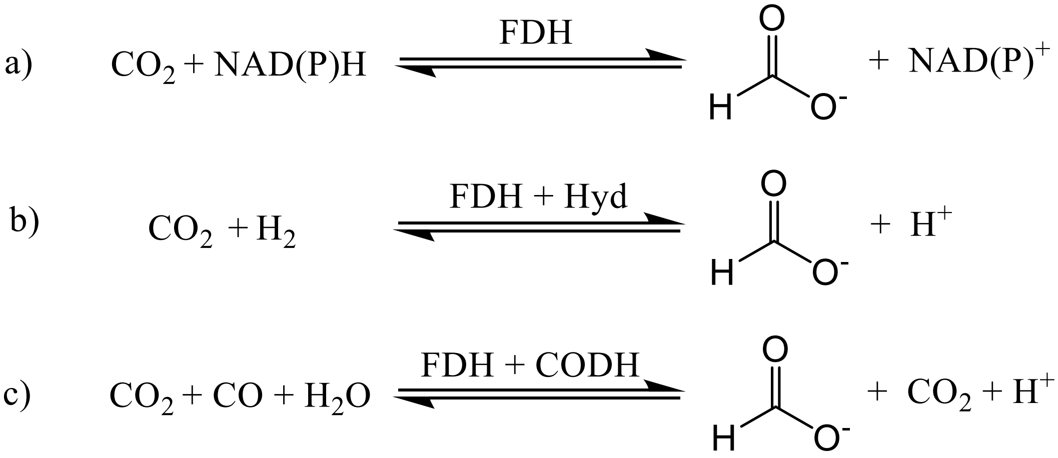
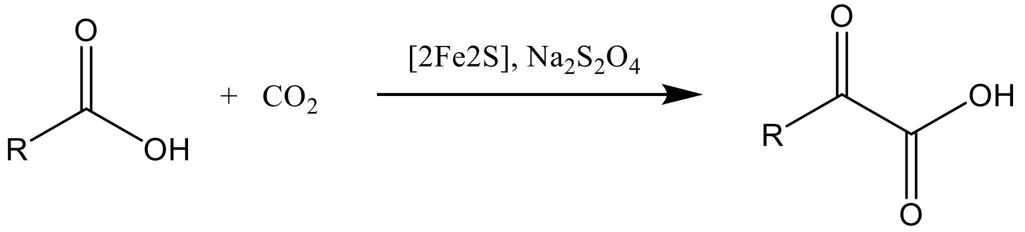


Figure 6



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