A.4 Chemistry of Weathering Processes

Introduction

Many weathering processes, including biodegradation, involve chemical transformation. In general, the same chemical principles apply whether a reaction occurs in the presence of air and sunlight, inside a refinery reactor, or inside a living organism. Without help (catalysis) the main hurdle for chemical transformation is the energy barrier known as "energy of activation" that stabilizes hydrocarbons. If complete oxidation to carbon dioxide is desired, providing enough terminal electron acceptors may present another challenge.

Redox Reactions

Complete oxidation of hydrocarbons requires a large number of electrons, because hydrocarbons represent the most reduced form of carbon. To turn all of their carbon atoms into CO_2, a large number of electrons will have to be accommodated elsewhere. The formal charge on the carbon in methane is –4 and –3 in the two carbon atoms of ethane. A formal charge of –2 could be assigned to the middle carbon atom of propane. Turning methane (CH_4) into carbon dioxide (formal charge +4) involves the transfer of eight electrons. Ethane (C_2H_6) transfers 14 electrons, propane (C_3H_8) 20 electrons, hexadecane ($C_{16}H_{34}$) 98 electrons, and octadecane ($C_{18}H_{38}$) 110 electrons upon complete oxidation. Electrons can be released only in the presence of electron acceptors such as oxygen molecules, which can accept four electrons each. Examples of other electron acceptors are oxygen-containing inorganic compounds such sulfate or manganate ions or partially oxidized organic molecules. Living organisms use redox coenzymes as "electron shuttles" to move one or two electrons at a time from electron donor to electron acceptor. Not all reactions that lead to oxidation products are redox reactions; combustion and photooxidation involve radicals.

Thermodynamics

Thermodynamics provides information on whether a reaction would be favorable based on whether it would result in a net gain or loss of energy and how much energy could theoretically be obtained under ideal conditions. Thermodynamic data tables often contain experimentally determined energies (heats) of combustion. Based on thermodynamics, hydrocarbons are expected to release a large amount of energy upon complete oxidation. However, thermodynamics does not predict whether a chemical will actually undergo a reaction.

Kinetics

Kinetics provides information on the rate or speed of a reaction and whether a reaction is feasible. All chemicals that are stable under ambient conditions must overcome an energy barrier to undergo any transformation. A low energy barrier means that the chemical can be coaxed fairly easily into reacting. Hydrocarbons are fairly inert chemically at ambient temperature and pressure (Widdel and Rabus 2001; Labinger and Bercaw 2002; Hostettler et al. 2007; Rabus et al. 2016). This means that their energy barriers are high and that significant amounts of energy and/or catalysts are required to activate them initially to undergo any type of chemical or biochemical reaction. Catalysts break down reactions with large energy barriers into multiple steps with smaller energy barriers. Catalysts used in refineries or engines are often made of certain metals and are fairly nonspecific, whereas catalysts used in biodegradation are microbial enzymes that are very specific. The likelihood of a particular type of hydrocarbon undergoing transformation depends on the energy of activation. The "energy of activation" (Figure A4-1) is a kinetic concept and not to be confused with the energy of the reaction, which is a thermodynamic concept.

Energy profiles, also called reaction diagrams or reaction coordinate diagrams, are often used to illustrate kinetic concepts. Figure A4-1 illustrates three scenarios: hydrocarbon combustion, complete oxidation by aerobic microorganisms, and partial oxidation by anaerobic organisms. The biological processes can be divided into many steps, each of which requires energy of activation. The energy of activation for each of the steps is smaller than that for the big step in combustion, which makes it possible for these reactions to occur under normal ambient conditions and inside of living organisms.
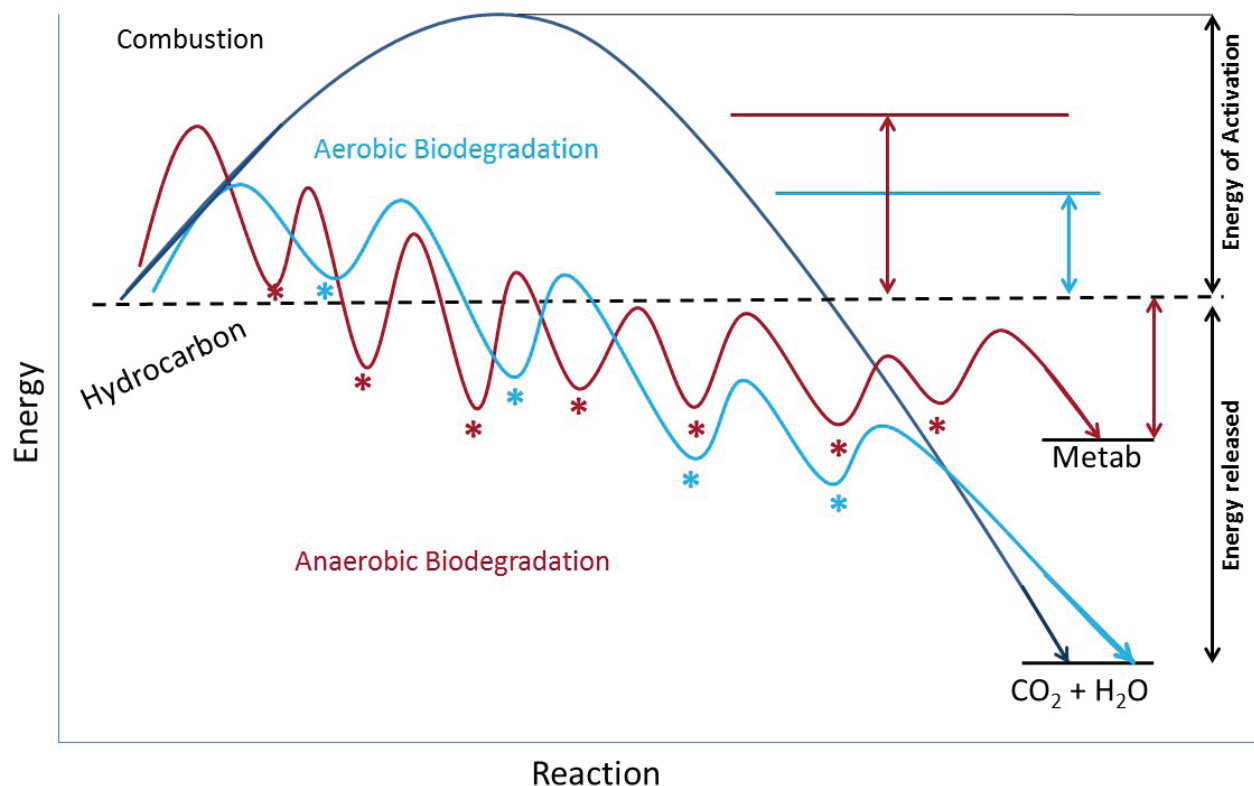
Figure A4-1. Kinetic strategies for the activation and degradation of hydrocarbons

This simple hypothetical reaction diagram provides a schematic illustration of the different kinetic strategies for the activation and degradation of hydrocarbons. Biodegradation is a type of chemical transformation that occurs in a stepwise manner and releases energy from hydrocarbons in small increments. The low-energy points marked with asterisks in the reaction paths for aerobic and anaerobic biodegradation represent metabolites.

Biochemical Reactions and Pathways

Biodegradation of a hydrocarbon always requires many steps, even when abundant oxygen is available. Aerobic degradation of an aliphatic hydrocarbon is typically initiated by the stepwise oxidation of a single carbon atom located on one end of the molecule to form a carboxylic acid, which is immediately esterified with a cellular factor to generate acyl-coenzyme A. Anaerobic processes can also generate acyl Co-A. This ester can undergo many rounds of β-oxidation and each round breaks off acetic acid units in the form of esters (Figure A4-2). There are many possible fates of the acetic acid units, especially under anaerobic conditions.

> ### *Fatty Acids*
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> Fatty acids are carboxylic acids that are found in all living organisms, where they have important functions. Many resemble aliphatic hydrocarbons with a COOH- (acyl-) group on one end. In cells, they often form esters.
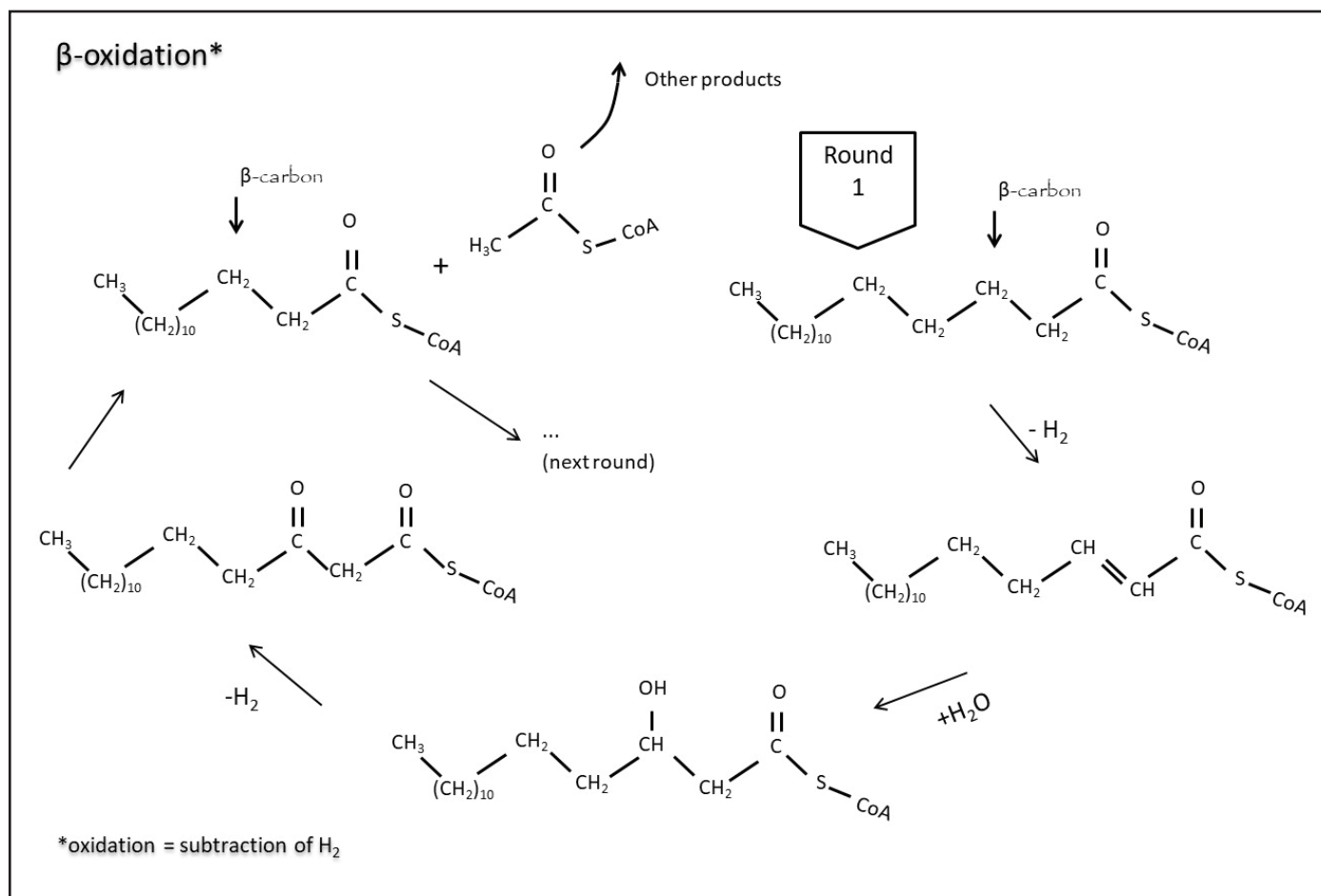
Figure A4-2. Beta-oxidation

This figure shows one round of β-oxidation, a widely used pathway for the degradation of many hydrocarbons after activation generates a terminal carboxylic acid. Oxidation occurs on the second or β-carbon from the acid group. The initial and final carboxylic acids are linked to coenzyme A, which is vitamin-derived thiol (alcohol with sulfur in place of oxygen) used for shuttling acids.

For maximum energy production, aerobic organisms feed acetyl-coenzyme A into the tricarboxylic acid (Krebs) cycle, which ultimately results in the generation of CO2 and energy. Alternative, acetyl-coenzyme A or the longer acyl-coenzyme A esters can be used for synthesis of new molecules, which facilitates growth of the microbial community and generation of biomass.

During anaerobic biodegradation of aliphatic as well as aromatic hydrocarbons the initial activation is the reaction with fumarate to generate succinates (Figure A4-3). The succinates are sometimes called "signature metabolites" and can be considered evidence of biodegradation (Beller, Ding, and Reinhard 1995; Young and Phelps 2005; Foght 2008; Agrawal and Gieg 2013; Rabus et al. 2016).

Coenzymes

Coenzymes help the main bio-catalysts (enzymes) by providing specific elements needed for a reaction such as electrons or functional groups. Many are derived from vitamins. Examples are redox coenzymes, which take electrons from oxidation reactions to where electrons are needed for reduction, or coenzyme A which temporarily binds organic acids at esters to facilitate their reuse by living organisms.
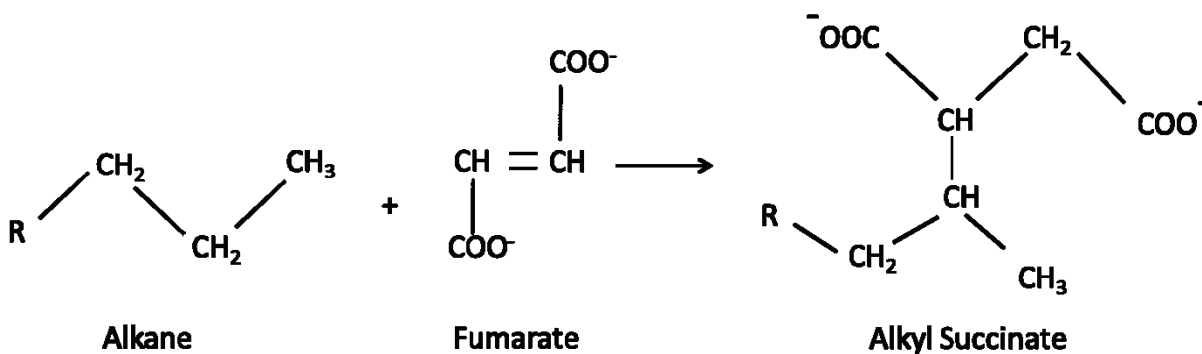
Figure A4-3. Fumarate addition for activation of alkanes

The reaction also activates toluene under anaerobic conditions (Young and Phelps 2005) (Figure A4-4). A number of benzenes and naphthalenes can be activated in this way following alkylation. However, there is no single, predominant pathway for the complete degradation of hydrocarbons under anaerobic conditions and many outcomes and products are possible, depending on site conditions, microbial consortia and structural features of a given hydrocarbon.

> ### *Pathway*
> A sequence of biochemical (enzyme-catalyzed) reactions that leads to a specific product. Example: A + B > C > D + 3E and D> F + G
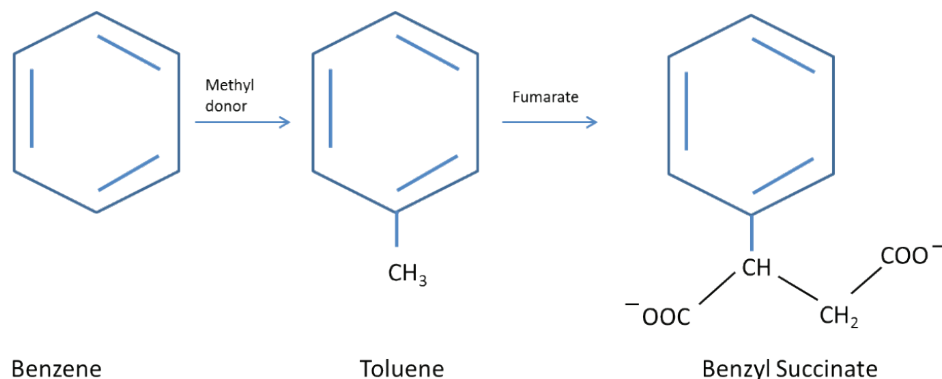

Figure A4-4. Generation of benzylsuccinate from toluene or from benzene that has been methylated

Formation of Metabolites

Stepwise petroleum degradation leads to partial breakdown products called "metabolites" or "polar compounds." The latter term is used to indicate that they are more water soluble than the parent hydrocarbons. The term "metabolite" implies that a compound was formed by a living organism through enzyme action. Most of the partial breakdown products associated with terrestrial releases are metabolites. Occasionally, the same or similar products are formed by photooxidation (see text box). Because these oxygen-containing compounds may be chemically indistinguishable, we often refer to all breakdown products as "metabolites." Intermediate metabolites are often more biologically active than the parent or starting compounds.

> ### *Biodegradation and photooxidation*
> These reactions can sometimes produce identical breakdown products even though the chemical strategies differ: Photooxidation requires multiple bonds and high energy (UV) light, while biodegradation requires the right overall (chemical and three-dimensional) structure so that a compound can bind to and interact with biological catalysts (enzymes), similar to a key fitting into a lock.

Signature Metabolites

Although many metabolites produced during the later stages of petroleum hydrocarbon breakdown may resemble naturally occurring molecules such as fatty acids, early metabolites have been identified that are clearly indicative of petroleum degradation. For example, succinyl adducts, which are formed by fumarate addition and are larger than the original hydrocarbons, are often the first readily detectable degradation intermediates of the anaerobic degradation of aliphatics as well as aromatics (Beller, Ding, and Reinhard 1995; Young and Phelps 2005; Foght 2008; Agrawal and Gieg 2013; Rabus et al. 2016).

Persistent Metabolites and Partial Hydrocarbon Breakdown Products

Structural factors determine whether it is more or less difficult to degrade a certain type of hydrocarbon. For example, hydrocarbons with double bonds are often more easily degraded than those with single bonds only. Molecules with double bonds and aromatic systems may be altered by photooxidation in the presence of light that contains the appropriate wavelength. Although PAHs are one of the groups that are more difficult to degrade, they provide some good examples of (partial) oxidation through different processes. Due to their unsaturated nature, they can absorb energy from sunlight for the initial activation. Because an environment with sunlight also has adequate levels of oxygen, oxidation can occur through simple chemical reactions. However, many PAH metabolites do not have the right electron structures to interact with light of the spectral composition of sunlight and further oxidation to CO_2 requires other mechanisms. An example of a PAH metabolite that can be generated either by photooxidation or biodegradation is anthraquinone (Figure A4-5), which can be produced during phenanthrene degradation.
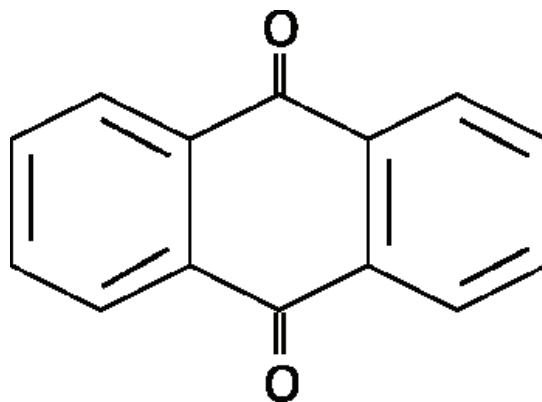
Anthraquinone

Figure A4-5. Anthraquinone—a degradation product of phenanthrene

Anthraquinone can be produced by photooxidation (Mallakin et al. 1999) or microbial degradation of phenanthrene (Moody et al. 2001).

Difficult-to-degrade hydrocarbons can sometimes be activated through co-metabolism (partial transformation together with another, similar hydrocarbon (Dalton and Stirling 1982)). This can produce dead-end metabolites, which are partially oxidized molecules that cannot be processed further (Foght 2008; Heider et al. 1999). Anthraquinone is an example of a dead-end metabolite. Because microorganisms have difficulty degrading dead-end metabolites, those compounds may persist in the environment. Persistent metabolites can accumulate and cause product repression or inhibit degradation of other molecules (Kazunga and Aitken 2000). Product repression occurs when the product of an enzymatic pathway (a series of enzymatic reactions) shuts down a pathway once it reaches a certain concentration. This has also been observed for alkane degradation (Rojo 2009).

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