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The bacterial catabolism of polycyclic aromatic hydrocarbons: Characterization of three hydratase-aldolase-catalyzed reactions[☆]



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Summary Polycyclic aromatic hydrocarbons (PAHs) are highly toxic, pervasive environmental pollutants with mutagenic, teratogenic, and carcinogenic properties. There is interest in exploiting the nutritional capabilities of microbes to remove PAHs from various environments including those impacted by improper disposal or spills. Although there is a considerable body of literature on PAH degradation, the substrates and products for many of the enzymes have never been identified and many proposed activities have never been confirmed. This is particularly true for high molecular weight PAHs (e.g., phenanthrene, fluoranthene, and pyrene). As a result, pathways for the degradation of these compounds are proposed to follow one elucidated for naphthalene with limited experimental verification. In this pathway, ring fission produces a species that can undergo a non-enzymatic cyclization reaction. An isomerase opens the ring and catalyzes a *cis* to *trans* double bond isomerization. The resulting product is the substrate for a hydratase-aldolase, which catalyzes the addition of water to the double bond of an

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α,β -unsaturated ketone, followed by a retro-aldol cleavage. Initial kinetic and mechanistic studies of the hydratase-aldolase in the naphthalene pathway (designated NahE) and two hydratase-aldolases in the phenanthrene pathway (PhdG and PhdJ) have been completed. Crystallographic work on two of the enzymes (NahE and PhdJ) provides a rudimentary picture of the mechanism and a platform for future work to identify the structural basis for catalysis and the individual specificities of these hydratase-aldolases.

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Introduction

Aromatic hydrocarbons are characterized by the presence of the very stable benzene ring (Scheme 1). Polycyclic aromatic hydrocarbons (PAHs) consist of multiple aromatic rings ranging from the simplest one, naphthalene (1, Scheme 1), to more elaborate ones such as phenanthrene (2), fluoranthene (3), and pyrene (4) (Kimes et al., 2014).

Microbial pathways for the degradation of benzene and derivatives such as toluene and xylene have been extensively characterized (Kimes et al., 2014). The meta-fission pathway (Scheme 2) is a major route for the bacterial catabolism of monocyclic compounds (Kimes et al., 2014; Manjasetty et al., 2003). Initially, the aromatic species (e.g., toluene) is converted to catechol (5), (or a derivative), which is subjected to ring cleavage adjacent to a hydroxyl group (as indicated). The ring opened compound, 2-hydroxymuconate semialdehyde (6), is then processed by a series of transformations to yield pyruvate and acetyl CoA (Manjasetty et al., 2003). The enzymes comprising this pathway and other degradation pathways for the monocyclic aromatic hydrocarbons have provided many significant insights into enzyme chemistry, specificity, and evolution.

The individual enzymes in the microbial catabolic pathways for PAHs are not as well characterized, if at all. Our interest in these pathways was sparked by the explosion of the Deepwater Horizon drilling rig and subsequent oil spill in the Gulf of Mexico (off the southeastern coast of the United States) in April 2010. An estimated 5 million barrels of crude oil were spilled in the Gulf before the oil well was finally capped about 3 months later. Thus far, the Deepwater Horizon oil spill and the Exxon Valdez oil spill (in 1989) are the two worst spills in the US, and are not expected to be the last major spills. In addition, there have been many smaller spills (Atlas and Hazen, 2011).

The lighter crude oil from the Gulf of Mexico is rich in low molecular weight hydrocarbons and in microorganisms that degrade these compounds. These organisms likely evolved this capability over the years as a result of the natural leakage of oil from the Gulf floor, estimated to be 1.4 million barrels of oil each year (Kimes et al., 2014). It has been suggested that microbial processes removed 43–61% of the oil spilled in the Deepwater Horizon accident (Joye, 2015). Although PAHs are minor components of lighter crude oil,

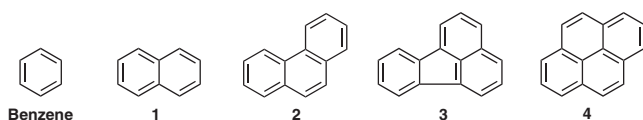
they are the most toxic. Moreover, the fate of PAHs in the Deepwater Horizon oil spill is less clear. For both reasons, it is necessary to have a better understanding of the microbial processes that degrade PAHs.

Characterization of PAH catabolic pathways

There is a considerable body of literature on the microbial degradation of PAHs including the identification of gene clusters, individual enzymes, and the demonstration that many bacterial species can completely catabolize these compounds to cellular metabolites. Examination of the proposed pathways suggests that one major strategy for the degradation of PAHs involves the successive removal of each ring by a round of four transformations. This strategy is illustrated by the naphthalene catabolic pathway, which is the most extensively characterized pathway for the degradation of a PAH.

In the proposed naphthalene catabolic pathway in *Pseudomonas putida* G7, two enzymes catalyze the dihydroxylation of one ring to yield 1,2-dihydroxynaphthalene, 7 (Scheme 3) (Eaton and Chapman, 1992). Subsequently, ring fission produces a chemically reactive dienol (8). Chemical ketonization of 8 generates 9, which reacts non-enzymatically to yield 2-hydroxychromene-2-carboxylate (10). The hemiketal 10 slowly converts to *trans*-*o*-hydroxybenzylidenepyruvate (11), but the glutathione-dependent enzyme, 2-hydroxychromene-2-carboxylic acid (HCCA) isomerase (designated NahD), accelerates this transformation. One single enzyme, *trans*-*o*-hydroxybenzylidenepyruvate hydratase-aldolase (designated NahE), then catalyzes two reactions: the addition of water to the double bond of 11 to afford 12, and the subsequent retro-aldol cleavage of 12 to produce salicylaldehyde (13) and pyruvate. Oxidation of salicylaldehyde generates salicylate, which is directed to the meta-fission pathway. In this way, naphthalene can be used as a sole source of carbon and energy for the organism.

Each ring of the high molecular weight species (e.g., phenanthrene, fluoranthene, and pyrene, 2, 3, and 4 in Scheme 1) is proposed to undergo a similar set of reactions, but many of these activities have not been experimentally confirmed (Kweon et al., 2011). In addition, the substrates and products are not known for some transformations and might have limited solubility. Nonetheless, the proposed transformations raise many interesting questions about mechanism, specificity, and evolution. The answers to these questions will provide a better understanding of the individual enzymatic transformations and assist in the optimization of the corresponding enzymes for bioremediation.



Scheme 1

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