Biological reductive dehalogenation of short-chain aliphatic halocarbons - possibilities and limits.

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1. Introduction

Several studies have shown that, under laboratory conditions, many chlorinated and also some fluorinated hydrocarbons, used in high amounts by industry, can be dehalogenated and even mineralized by bacteria at considerable rates[1,2,3,4]. In the following, a short review of the dehalogenation mechanisms for technically relevant halogenated methanes, ethanes and ethenes will be presented, with special emphasis on reductive dehalogenation. Furtheron, the possibilities and problems of a technical application of these processes will be discussed.

2. Metabolic dehalogenation by aerobic bacteria

Short-chain aliphatic halocarbons (SCAH) with only one or two chlorine substituents are good growth and energy substrates for aerobic bacteria, such as certain species of Pseudomonas, Hyphomicrobium, Arthrobacter and Xanthobacter[5]. Some of them can be utilized as the only carbon and energy source (e.g. dichloromethane, 1,2-dichloroethane, vinyl chloride). Hydrolysis is the main dehalogenation mechanism. The dehalogenation of 1,2-dichloroethane for example is catalyzed by two different halidohydrolases[5]. The xenobiotic compounds are degraded with considerable rates. Dichloromethane e.g. is degraded at a rate of about 20 nm. $\text{min}^{-1}.\text{mg}^{-1}$ protein by mixed cultures[6]. Together with high specifities of the dechlorinating enzymes, these characteristics are good prerequisites for a technical application.

3. Cometabolic dehalogenation by aerobic bacteria

A second dehalogenation process is catalysed by mono- and dioxygenases with broad substrate spectrum[6]. These enzyme systems transform SCAHs without being able to utilize them. All the oxygenases form toxic epoxides, inhibiting the dechlorinating bacteria during the oxidation of the SCAHs[7]. Among others, this disadvantage might have been responsible for the lack of technical application of the cometabolic dechlorination.

4. Reductive dehalogenation by anaerobic bacteria

Due to thermodynamical reasons highly chlorinated hydrocarbons are expected to be more easily or exclusively dechlorinated under anaerobic conditions[8]. Tetrachloroethene (PCE), for example, is persistent under aerobic conditions. Under strictly anaerobic conditions and in the presence of a suitable electron donor, however, this compound is reductively dechlorinated at high rates[1,3,9]. Usually low-chlorinated metabolites, such as cis-1,2-dichloroethene and vinyl chloride, accumulate during this process due to decreased reduction rates for the chlorinated intermediates. At least two different anaerobic bacterial species are involved in the complete dehalogenation of PCE to ethene. The first species produces cis-1,2-dichloroethene (DCE) from PCE, the second dehalogenates DCE to ethene or ethane. Recently a PCE-dehalogenating bacterium, Dehalobacter restrictus, had been isolated by Holliger[10]. This organism depends on PCE as electron acceptor.

Up to now little is known about the mechanism of anaerobic dehalogenation reactions. Results had been obtained recently showing that non-enzymic reactions, catalysed by porphinoid coenzymes (e.g. corrinoids and coenzyme F 430, the prosthetic group of the methyl coenzyme M reductase) may be responsible for non-specific biological dehalogenations[10].

Similar to the cometabolic oxidation of chlorinated hydrocarbons catalysed by non-specific monooxygenases, no carbon or energy is gained during the reductive dechlorinations catalysed by porphinoid coenzymes. Recently, however, microorganisms have been enriched or isolated which productively utilize SCAHs like methyl chloride[4] and dichloromethane[11] under strictly anaerobic conditions. These results indicate that, in addition to non-enzymic reactions, new anaerobic processes to degrade SCAHs have been developed by certain bacteria.

5. Discussion

Many of the technically produced SCAHs are xenobiotic compounds which are quite new to biological systems. Nevertheless, bacteria possess several mechanisms to transform such substances. The existence of biological degradation mechanisms does not mean that SCAHs are no problem to nature. Even if a substance has been proven to be easily degradable under laboratory conditions, it may persist under natural conditions[12]. Antagonistic interactions between different pollutants in a contaminated environment and a number of other environmental conditions (e.g. redox potential, availability of inorganic and organic nutrients, absence or presence of inhibitors) influence the fate of an organic compound. This poses great demands on the technical processes used to remediate contaminated soils and groundwaters. At present, technical processes have been developed for the biological elimination of two chlorinated organic solvents: dichloromethane and 1,2-dichloroethane[6,13].

No biological processes are presently available to purify water contaminated with polychlorinated hydrocarbons. One of the most frequently found contaminants in polluted groundwater is PCE. This highly chlorinated hydrocarbon is persistent under aerobic conditions. Due to the accumulation of toxic metabolites such as vinyl chloride during the anaerobic dechlorination of PCE, a direct application of reductive dehalogenation is not feasable. A two-step treatment based on anaerobic degradation of PCE followed by aerobic degradation of vinyl chloride and other low-chlorinated compounds can be a satisfactory procedure.

6. References

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