

Anaerobic Coupling Reactions between Reduced Intermediates of 2,4-Dinitroanisole (DNAN)

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Background/Objectives. 2,4-Dinitroanisole (DNAN) is a nitroaromatic compound that is gradually replacing trinitrotoluene (TNT) in military explosives. DNAN, an insensitive munition, is safer than TNT because it is less prone to unintentional detonation. Consequently, it does not fully combust, and leaves behind a significant amount of residue on firing ranges. This residue may then enter the soil and groundwater during rainfall events. Anaerobic bacteria in waterlogged soils, for example, are known to reduce nitroaromatics to their corresponding aromatic amines. The widely accepted fate is that these aromatic amines react with oxidized soil minerals and/or O_2 to form radicals that (co)polymerize with each other and/or phenolic moieties present in the soil. Preliminary research has shown that anaerobic conditions lead nitroaromatics to a different fate. We hypothesize that reduced intermediates of nitroaromatics, in particular nitrosoaromatics and aromatic amines, couple with each other via nucleophilic substitution to form azo-bonded dimers and oligomers. In the absence of O_2 , it is also possible that amino groups of reduced nitroaromatics react with quinone moieties in soil humus to form adducts. This effectively immobilizes these toxic reduced intermediates and coupling products. The objective of this study is to elucidate the coupling reactions between reduced intermediates of DNAN and gain further insight into the fate of nitroaromatic compounds in anaerobic environments.

Approach/Activities. 4-Nitroanisole was chosen as a model compound for the more complex DNAN. To study the overall process of biological reduction and chemical coupling, 4-nitroanisole was spiked gradually into incubations of anaerobic granular sludge from a brewery. These experiments were carried out in a mineral medium flushed free of O_2 and supplied with H_2 as the electron donor. Azo dimer formation was compared with that of a set of controls and with a commercially-available standard. An ultra-high performance liquid chromatograph coupled to a diode-array detector and a mass spectrometer were used to analyze the chemical species and search for additional coupling products and metabolites. Experiments pairing 4-nitrosoanisole with 4-aminoanisole in the absence of O_2 and inoculum to study the nucleophilic coupling mechanism described above are in progress. Adduct formation between 4-aminoanisole and 1,4-benzoquinone is also being studied as a model of the coupling between amino groups on aromatic compounds and soil quinone moieties.

Results/Lessons Learned. The azo dimer 4,4'-dimethoxyazobenzene was formed in the incubation of 4-nitroanisole with anaerobic granular sludge, as verified by liquid chromatography, UV-Vis spectroscopy, and mass spectrometry. However, the azo bond was not stable in the sludge incubations, and the dimer did not accumulate. Other, uncharacterized suspected coupling products formed and accumulated in this experiment, although the major product was 4-aminoanisole. A similar approach as described above will be taken to study anaerobic coupling reactions with DNAN as the starting material. Because DNAN has two nitro groups, the number of possible dimers and oligomers that can form is theoretically much higher than with 4-nitroanisole. The additional amino groups on reduced DNAN intermediates and coupling products are expected to enhance their incorporation into soil humus.