

DOWNLOAD PDF BIODEGRADATION OF NITROAROMATIC COMPOUNDS AND EXPLOSIVES

Chapter 1 : Biodegradation of Nitroaromatic Compounds and Explosives : Hans-Joachim Knackmuss :

Biodegradation of Nitroaromatic Compounds and Explosives gives you a synthesis of ongoing research and an appreciation of the remarkable range of biochemical strategies available for the transformation of nitroaromatic compounds.

Only few aromatic compounds, bearing one nitro group as a substituent of the aromatic ring, are produced as secondary metabolites by microorganisms. The majority of nitroaromatic compounds in the biosphere are industrial chemicals such as explosives, dyes, polyurethane foams, herbicides, insecticides and solvents. Detection of unrecovered land mines is a growing international problem. Unrecovered land mines are a legacy that continues to harm people long after the hostilities cease. The most widely used tool for land mine detection today is the hand-held metal detector. Other methods for landmine detection are limited due to their high false alarm rate. Chemical sensors have been investigated for mine detection. For chemical species having favorable spectral properties, remote sensing can be achieved by fluorescence light detection and ranging LIDAR. Nitroaromatic explosives exhibit strong ultraviolet absorption but low fluorescence, thus direct detection is not practical. Indirect detection in soil can be obtained using a synthetic chemical polymer that exhibits a change in fluorescence in the presence of an explosive compound. Penetration of nitroaromatic compounds through the skin is a major concern for the military. An important characteristic of nitroaromatic compounds is their ability to rapidly penetrate the skin. They can cause the formation of methemoglobin on acute exposures and anemia on chronic exposures. Additionally, local irritation, liver damage and bladder tumors have also been identified. These compounds are generally recalcitrant to biological treatment and remain in the biosphere, where they constitute a source of pollution due to both toxic and mutagenic effects on humans, fish, algae and microorganisms. The best-known nitroaromatic compound is the explosive TNT 2,4,6-trinitrotoluene. The optimal remediation strategy for nitroaromatic compounds depends on many site-specific factors. Composting and the use of reactor systems lend themselves to treating soils contaminated with high levels of explosives. Compared to composting systems, bioreactors have the major advantage of a short treatment time, but the disadvantage of being more labour intensive and more expensive. TNT is classified as a secondary explosive because it is less susceptible to initiation and requires a primary or initiating explosive to ignite it. TNT can be used as a booster or as a bursting charge for high-explosive shells and bombs. The advantages of TNT include low cost, safety in handling, fairly high explosive power, good chemical and thermal stability, compatibility with other explosives, a low melting point favorable for melt casting operations and moderate toxicity. TNT is a crystalline substance. The importance of TNT as a military explosive is based upon its relative safety in manufacture, loading, transportation, and stowage, and upon its explosive properties. Manufacturing yields are high and production relatively economical. The chemical names for TNT are trinitrotoluene and trinitrotol. TNT is toxic, odorless, comparatively stable, nonhygroscopic, and relatively insensitive. When the proportion of impurities is much greater, the color is darker, often brown, and the chemical is known as grade B TNT. It may be ignited by impact, friction, spark, shock, or heat. TNT does not form sensitive compounds with most metals. The melting point varies between 102 and 104 °C. TNT does not appear to be affected by acids but is affected by alkalies lye, washing soda, and so on, becoming pink, red, or brown, and more sensitive. It is practically insoluble in water, but soluble in alcohol, ether, benzene, carbon disulfide, acetone, and certain other solvents. The velocity of detonation is approximately 22,000 ft/s. Exudate has been known to separate from cast TNT. It may appear pale yellow to brown and may vary in consistency from an oily liquid to a sticky substance. The amount and rate of separation depend primarily upon the purity of the TNT and, secondarily, upon the temperature of the stowage place. Grade B low-melting point TNT may exude considerable liquid and generate some gas. This exudation is accelerated with an increase in temperature. Pure TNT will not exude since exudate consists of impurities that have not been extracted in the refining process. Exudate is a mixture of lower melting isomers of TNT,

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nitrocompounds of toluene of lower nitration, and possible nitrocompounds of other aromatic hydrocarbons and alcohols. It is flammable and has high sensitivity to percussion when mixed with absorbents. Its presence does no appreciable harm to the stability but somewhat reduces the explosive force of the main charge. In some ammunition, an inert wax pad is used in the loading operation, and, in some cases, waxy material may ooze from the case. It should not be confused with the TNT exudate previously described. This material should, however, be tested for TNT to confirm its actual composition, TNT exudate, when mixed with a combustible material, such as wood chips, sawdust, or cotton waste, will form a low explosive that is highly flammable and ignites easily from a small flame. It can be exploded in a reamer similar to a low grade of dynamite, but the main danger is its fire hazard. Accumulation of exudate is considered a great risk of explosion and fire. Its accumulation should always be avoided by continual removal and disposal as it occurs. These stocks should be identified and checked periodically for the presence of exudate. The exudate is soluble in acetone or alcohol. One of these solvents requiring adequate ventilation or clean, hot water should be used to facilitate removal and disposal of the exudate. Under no circumstances should soap or other alkaline preparations be used to remove this exudate. During production TNT is in the form of a liquid which is then cooled and washed with water to form solid flakes in the form of colorless crystals, though commercial crystals are yellow. The flakes can be remelted at low temperatures degrees Fahrenheit and poured into munitions shells and casings. TNT was widely used by the military because of its low melting point and its resistance to shock or friction which allows it to be handled, stored, and used with comparative safety. Deaths from aplastic anemia and toxic hepatitis were reported in TNT workers prior to the s. With improved industrial practices, there have been few reports of fatalities or serious health problems related to its use. Exposures at or below 0. Among some groups of workers, there is a reduction in average hemoglobin and hematocrit values. Workers deficient in glucosephosphate dehydrogenase may be particularly at risk of acute hemolytic disease. Three such cases occurred after a latent period of 2 to 4 days and were characterized by weakness, vertigo, headache, nausea, paleness, enlarged liver and spleen, dark urine, decreased hemoglobin levels, and reticulocytosis. Although no simultaneous measurements of atmospheric levels were available, measurement on other occasions showed exposure levels up to 3. Cataracts are also reportedly produced with chronic exposures for more than 5 years. The opacities did not interfere with visual acuity or visual fields. The induced cataracts may not regress once exposure ceases, although progression is arrested. The vapor or dust can cause irritation of mucous membranes resulting in sneezing, cough, and sore throat. Although intense or prolonged exposure to TNT may cause some cyanosis, it is not regarded as a strong producer of methemoglobin. Other occasional effects include leukocytosis or leukopenia, peripheral neuritis, muscular pains, cardiac irregularities, and renal irritation. Trinitrotoluene is absorbed through skin fairly rapidly, and reference to airborne levels of vapor or dust may underestimate total systemic exposure if skin exposure also occurs. Apparent differences in dose-response relationships based only on airborne levels may be explained by differences in skin contact. TNT causes sensitization dermatitis; the hands, wrist, and forearms most commonly are affected, but skin at friction points such as the collar line, belt line, and ankles also is often involved. Erythema, papules, and an itchy eczema can be severe. The skin, hair, and nails of exposed workers may be stained yellow. Hyperplasia and carcinoma of the urinary bladder also were observed in female rats. Historically, control of exposure to TNT has been accomplished through general safety and hygiene measures, yet additional, specific measures are necessary. The Hazard Communication Program, for example, should instruct workers about the need for strict personal and shop hygiene, and about the hazards of the particular operations that are conducted in that plant. Furthermore, respiratory protection equipment should be selected according to NIOSH guidance, and should be worn during operations that release dust, vapor, or fumes. Before WWII, research suggested that improving the nutritional status of TNT workers might help improve their resistance to toxic effects. TNT interacts with certain medications - including isoniazid, phenylbutazone, phenytoin, and methotrexate. Anyone taking these medications while working with TNT should be closely followed by the occupational physician. Army currently recommends preplacement and periodic semiannual

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examinations of TNT workers. In some studies, evidence of liver toxicity, changes in blood cell production, and cataracts were noted when exposure levels ranged below 0. Skin absorption has also been noted to be a significant means of exposure in several studies. Dermal exposure over an 8 hour period cannot be readily quantitated at a worksite, however use of protective clothing to include head cover and impermeable gloves is essential to prevent skin absorption of TNT. DNT is not a natural substance but rather is usually made by reacting toluene a solvent with mixed nitric and sulfuric acids, which are strong acids. DNT is used to produce flexible polyurethane foams used in the bedding and furniture industry. DNT is also used to produce ammunition and explosives and to make dyes. It is also used in the air bags of automobiles. It has been found in the soil, surface water, and groundwater of at least hazardous waste sites that contain buried ammunition wastes and wastes from manufacturing facilities that release DNT. DNT does not usually evaporate and is found in the air only in manufacturing plants. DNT also does not usually remain in the environment for a long time because it is broken down by sunlight and bacteria into substances such as carbon dioxide, water, and nitric acid. Workers who have been exposed to 2,4-DNT showed a higher than normal death rate from heart disease. However, these workers were exposed to other chemical as well. One study showed that male workers exposed to DNT had reduced sperm counts, but other studies did not confirm this finding. TNB 1,3,5-Trinitrobenzene The synthetic compound 1,3,5-TNB is used as a high explosive for commercial mining and military use, as a narrow-range pH indicator and as an agent to vulcanize natural rubber. The compound is a manufacturing by-product of the explosive, TNT, and is released to the environment in discharged wastewater. Additionally, any TNT itself that is present in the waste stream may be degraded to 1,3,5-TNB by photolysis under certain conditions of pH and organic matter content. The compound has a close structural relationship with the most widely produced military explosive, trinitrotoluene TNT , of which it is a manufacturing by-product and an environmental degradation product.

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Chapter 2 : Biodegradation of Nitroaromatic Compounds and Explosives - PDF Free Download

Summary: Nitroaromatic compounds are relatively rare in nature and have been introduced into the environment mainly by human activities. This important class of industrial chemicals is widely used in the synthesis of many diverse products, including dyes, polymers, pesticides, and explosives.

Includes bibliographical references and index. United States Air Force. Office of Scientific Research. Defense Threat Reduction Agency. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use. Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage or retrieval system, without prior permission in writing from the publisher. The consent of CRC Press LLC does not extend to copying for general distribution, for promotion, for creating new works, or for resale. Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation, without intent to infringe. The resulting discoveries have dramatically extended our knowledge about the strategies used by biological systems for dealing with such compounds. In addition, the basic research has provided a foundation for a number of practical applications of biological systems for destruction of nitroaromatic contaminants. In the advances in basic understanding of microbial degradation of nitroaromatic compounds were summarized in a book of reviews written by a group of experts in biochemistry, microbiology, and soil chemistry. Since that time the fundamental understanding has led to several practical applications involving biodegradation of nitroaromatic compounds previously thought to be recalcitrant to biological transformation. The symposium brought together a wide range of scientists and engineers to discuss not only basic advances, but also field applications based on biodegradation and biotransformation of nitroaromatic compounds and explosives. The invited speakers were asked to critically review recent advances in their areas of expertise and to describe how the basic work has led to practical applications. They were also asked to discuss the questions that remain to be answered by future research. Some of the areas still involve mostly basic research on biochemistry and microbiology, whereas in other areas there is a considerable amount of experience in field applications. The first goal of this book is to provide the reader with a timely synthesis of ongoing recent research and an appreciation for the remarkable range of biochemical strategies available for the transformation of nitroaromatic compounds. The second goal is to give a realistic evaluation of the current and potential field applications of the various strategies. Each chapter is designed to stand alone, thus there is occasionally some overlap in the introductory material and some experiments have been used as examples in more than one chapter. The book should be of interest to microbiologists, biochemists, engineers, and anyone concerned about the environmental behavior and destruction of nitroaromatic compounds and explosives. Chapter 1 provides a brief introduction and overview of the scope of the problem with environmental contamination by nitroaromatic compounds. Most of the incentive for research in the U. The extent of such contamination in much of the rest of the world is not known. The second chapter describes the strategies used by aerobic bacteria for converting nitroaromatic compounds into sources of carbon and energy. Most of the catabolic pathways are well understood, and there is a growing body of knowledge on the molecular biology of such systems. In addition, bacteria that grow on nitroaromatic compounds have been used in a variety of pilot- and field-scale applications. Chapter 3 examines the biochemistry and molecular biology of nitroarene dioxygenases, key enzymes that initiate the productive metabolism of a variety of substrates. Chapter 4 introduces more complex molecules that cannot serve as growth substrates for microorganisms, but, nonetheless, can be extensively transformed and detoxified by binding to soil. The exciting advances in the biochemistry of the initial enzymatic attack on polynitroaromatic compounds are described in detail along with the mechanisms of binding of the

intermediates to soil humic material. Enzymes that attack the aromatic ring of picric acid can lead to the elimination of nitrite and subsequent mineralization. In contrast, enzymes that reduce the nitro groups of nitrotoluenes can produce intermediates that bind to soil under appropriate conditions. Both strategies can lead to effective solutions for environmental contamination. Very recent discoveries, described in Chapter 5, reveal the sequences and arrangement of the genes involved in the bacterial degradation of picric acid. The work also illustrates the remarkable effectiveness of mRNA differential display in the discovery of genes involved in the degradation pathway and how the information has led to elucidation of the pathway. Simple nitrophenols and nitrobenzoates were the first nitroaromatic compounds discovered to be degraded by bacteria. Chapter 6 describes the recent advances in understanding the molecular biology of the degradative pathways of simple polar nitroaromatic compounds and their relationships to other catabolic sequences. Chapter 7 provides an overview of the current understanding of the biotransformation of nitroglycerin. Because the molecule is a nitrate ester rather than a nitroaromatic compound, the reductase enzymes that catalyze the initial attack on the molecule can cause the elimination of nitrite. This chapter also describes the remarkable discovery that the bacterial nitrate ester reductase can catalyze the elimination of nitrite from a wide range of nitro-substituted compounds, including TNT. Although many workers have reported the reduction of nitro groups of explosives by anaerobic bacteria, most of the work has been done with complex mixed cultures where it is impossible to study the details of the biochemistry of the transformation pathways. In contrast, Chapter 8 describes the details of TNT transformation by *Clostridium* and the central, previously unexpected, role of hydroxylamino derivatives as key intermediates. Fungi are the only organisms capable of significant amounts of TNT mineralization. The ligninolytic enzymes of *Phanerochaete chrysosporium* have been studied extensively because of their ability to transform TNT. Unfortunately, *Phanerochaete* does not grow well in soil and is inhibited by high concentrations of TNT. The authors of Chapter 9 have evaluated the TNT degradation abilities of a wide range of fungi adapted to a variety of habitats and discovered several that have considerable potential for use in practical applications. Phytoremediation is becoming widely accepted as a strategy for remediation of contaminated water and soil. Chapter 10 explores the recent advances in understanding transformation pathways based on studies with plant cell cultures, intact plants, and phytoremediation systems in the field. In Chapter 11, the author summarizes the previous understanding of the degradation mechanisms and then outlines some very recent discoveries that provide new insight about the reactions leading to mineralization by bacteria. Some of the newly proposed reactions differ considerably from the ones that have been accepted for many years. Most of the interest in biodegradation of nitroaromatic compounds stems from concerns about their fate and transport in the environment. Studies of biodegradation in complex natural systems are meaningless without a good understanding of the many abiotic reactions that affect the transformation and behavior of nitroaromatic molecules. Chapter 12 explains the abiotic transformations of the nitro substituents as well as the geomicrobiology involved in generation of the materials that interact with nitro compounds. Chapters 13 and 14 illustrate how the basic research in the past has led to practical treatment strategies based on composting and other large-scale systems. Composting has been the most extensively used approach to field-scale treatment of excavated soil. It is widely accepted in the U. Chapter 13 explains the basic understanding of the composting process and the state of the art in application. Chapter 14 describes the scope of the explosives contamination problem in the U. The comparison reveals that several technologies can be effective and relatively inexpensive for destruction of TNT in excavated soil. The authors would like to thank Alice Giraitis for outstanding editorial assistance and Loreen Kollar of the Florida State University Institute for International Cooperative Environmental Research for organizing the symposium. The authors also thank Shirley Nishino for taking on all the extra tasks required to make this book possible. Much of the work described in this book would not have been possible without the unfailing support of Walter Kozumbo of the U. Air Force Office of Scientific Research. He developed an outstanding basic research program to shed light on the strategies used by biological systems to detoxify and destroy nitroaromatic compounds. He provided funding for a number of outstanding investigators to work in critical areas and is responsible to a

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large extent for the recent exciting advances in the field. Spain has a B. For the past 20 years he has studied the mechanisms of biodegradation of synthetic organic compounds. He worked on the biodegradation of pesticides for five years at the U. Spain is responsible for both basic and applied research on the application of biotechnology for degradation and synthesis of organic compounds. He has organized several international symposia and edited a previous book on the biodegradation of nitroaromatic compounds and explosives. He has published extensively on the pathways involved in the biodegradation of a variety of nitroaromatic compounds and has also conducted a considerable amount of field work in the area. He received his B. Hughes attended graduate school at the University of Iowa. He joined the faculty of Rice University immediately thereafter. Much of his most recent research has dealt with the metabolism of nitroaromatic compounds, which have complex environmental chemistry. Specifically, his research group is trying to understand the pathways of metabolism and to identify the intermediates and products of metabolism. His work has relied heavily on the use of modern isolation and structural identification methods to define intermediates and products from complex mixtures of organic compounds. Hans-Joachim Knackmuss obtained his education as a diploma chemist and his degree of doctor rerum naturarum from the University of Heidelberg. In he was appointed full professor for microbiology at the University of Wuppertal and at the University of Stuttgart since Newman, and Lynda L. Williams and Neil C. Hughes Chapter 9 Fungal Degradation of Explosives: Shanks, and Phillip L. Jerger and Patrick M. Spain Explosives and other nitrated compounds Figure 1. Nitroaromatic pesticides such as dinoseb, dinitrocresol, parathion, and methylparathion are intentionally released in soil and water worldwide. They are also spilled accidentally at loading facilities and during agricultural use. Nitrophenols and nitrotoluenes are used extensively as feedstocks in industry and are often released to surface water in waste streams. The pesticides and simple nitroaromatic compounds are biodegradable by soil bacteria and do not accumulate in the environment unless concentrations exceed the assimilative capacity of the ecosystem. In contrast, explosives such as 2,4,6-trinitrotoluene TNT , hexahydro-1,3,5-trinitro-1,3,5-triazine RDX , and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine HMX are less biodegradable and often persist for extended periods in soil or groundwater. The major explosives manufacturing, handling, and storage sites in the U. Fortunately, most of the sites are owned by the U. A number of the sites have been cleaned up, and many are in the process of cleanup. Major exceptions include Volunteer and Ravenna Army Ammunition Plants where contamination is extensive and cleanup of contaminated soil and groundwater has not started. A substantial amount of dinitrotoluene-contaminated soil also remains at the Badger Army Ammunition Plant. The most recent public document on the scope of the problem¹ describes a timeline for the cleanup of contaminated soil at many of the sites, but does not provide information about contaminated groundwater. More detailed information about the scope of the problem and the current cleanup strategies is provided in Chapter In Germany, the situation is more problematic because many of the explosives manufacturing facilities Figure 1.

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Chapter 3 : Nitroaromatic Compounds, from Synthesis to Biodegradation

biodegradation and biotransformation of nitroaromatic compounds and explosives. The invited speakers were asked to critically review recent advances in their areas of expertise and to describe how the basic work has led to practical applications.

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productive metabolism of a variety of substrates. The insight about both the catalytic mechanism and the evolutionary origin of the enzymes provides a sense of how productive pathways might have evolved for organic compounds that have only been in the biosphere for a brief time. Chapter 4 introduces more complex molecules that cannot serve as growth substrates for microorganisms, but, nonetheless, can be extensively transformed and detoxified by binding to soil. The exciting advances in the biochemistry of the initial enzymatic attack on polynitroaromatic compounds are described in detail along with the mechanisms of binding of the intermediates to soil humic material. Enzymes that attack the aromatic ring of picric acid can lead to the elimination of nitrite and subsequent mineralization. In contrast, enzymes that reduce the nitro groups of nitrotoluenes can produce intermediates that bind to soil under appropriate conditions. 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In Chapter 11, the author summarizes the previous understanding of the degradation mechanisms and then outlines some very recent discoveries that provide new insight about the reactions leading to mineralization by bacteria. Some of the newly proposed reactions differ considerably from the ones that have been accepted for many years. Most of the interest in biodegradation of nitroaromatic compounds stems from concerns about their fate and transport in the environment. Studies of biodegradation in complex natural systems are meaningless without a good understanding of the many abiotic reactions that affect the transformation and behavior of nitroaromatic molecules. Chapter 12 explains the abiotic transformations of the nitro substituents as well as the geomicrobiology involved in generation of the materials that interact with nitro compounds. 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be effective and relatively inexpensive for destruction of TNT in excavated soil. The authors would like to thank Alice Giraitis for outstanding editorial assistance and Loreen Kollar of the Florida State University Institute for International Cooperative Environmental Research for organizing the symposium. The authors also thank Shirley Nishino for taking on all the extra tasks required to make this book possible. Much of the work described in this book would not have been possible without the unfailing support of Walter Kozumbo of the U. Air Force Office of Scientific Research. He developed an outstanding basic research program to shed light on the strategies used by biological systems to detoxify and destroy nitroaromatic compounds. He provided funding for a number of outstanding investigators to work in critical areas and is responsible to a large extent for the recent exciting advances in the field. Spain has a B. For the past 20 years he has studied the mechanisms of biodegradation of synthetic organic compounds. He worked on the biodegradation of pesticides for five years at the U. Spain is responsible for both basic and applied research on the application of biotechnology for degradation and synthesis of organic compounds. He has organized several international symposia and edited a previous book on the biodegradation of nitroaromatic compounds and explosives. He has published extensively on the pathways involved in the biodegradation of a variety of nitroaromatic compounds and has also conducted a considerable amount of field work in the area. He received his B. Hughes attended graduate school at the University of Iowa. He joined the faculty of Rice University immediately thereafter. Much of his most recent research has dealt with the metabolism of nitroaromatic compounds, which have complex environmental chemistry. Specifically, his research group is trying to understand the pathways of metabolism and to identify the intermediates and products of metabolism. His work has relied heavily on the use of modern isolation and structural identification methods to define intermediates and products from complex mixtures of organic compounds. Hans-Joachim Knackmuss obtained his education as a diploma chemist and his degree of doctor rerum naturarum from the University of Heidelberg. In he was appointed full professor for microbiology at the University of Wuppertal and at the University of Stuttgart since Besides being a university professor, he was a collaborator and advisor of the Bayer AG, Leverkusen "€", and since he has been head of the Department of Chemical Microbiology at the Fraunhofer Institute for Interfacial Engineering and Biotechnology in Stuttgart. He published about papers, largely on the biodegradation of xenobiotic compounds. His current research interest focuses on the elimination of xenobiotics from waste water, soil and exhaust gases, the design of new biodegradable synthetic products, and the development of new synthons by regio-, stereo-, and enantioselective biotransformation. Process Discovery to Field Application Newman, and Lynda L. Williams and Neil C. Hughes Chapter 9 Fungal Degradation of Explosives: Shanks, and Phillip L. From Basic Research to Field Application Jerger and Patrick M. Spain Explosives and other nitrated compounds Figure 1. Nitroaromatic pesticides such as dinoseb, dinitrocresol, parathion, and methylparathion are intentionally released in soil and water worldwide. They are also spilled accidentally at loading facilities and during agricultural use. Nitrophenols and nitrotoluenes are used extensively as feedstocks in industry and are often released to surface water in waste streams. The pesticides and simple nitroaromatic compounds are biodegradable by soil bacteria and do not accumulate in the environment unless concentrations exceed the assimilative capacity of the ecosystem. In contrast, explosives such as 2,4,6-trinitrotoluene TNT , hexahydro-1,3,5-trinitro-1,3,5-triazine RDX , and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine HMX are less biodegradable and often persist for extended periods in soil or groundwater.

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Chapter 4 : Explosives - Nitroaromatics

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Parales Find articles by Rebecca E. Nitroaromatic compounds are relatively rare in nature and have been introduced into the environment mainly by human activities. This important class of industrial chemicals is widely used in the synthesis of many diverse products, including dyes, polymers, pesticides, and explosives. Unfortunately, their extensive use has led to environmental contamination of soil and groundwater. The nitro group, which provides chemical and functional diversity in these molecules, also contributes to the recalcitrance of these compounds to biodegradation. The electron-withdrawing nature of the nitro group, in concert with the stability of the benzene ring, makes nitroaromatic compounds resistant to oxidative degradation. Recalcitrance is further compounded by their acute toxicity, mutagenicity, and easy reduction into carcinogenic aromatic amines. Nitroaromatic compounds are hazardous to human health and are registered on the U. Although the majority of these compounds are synthetic in nature, microorganisms in contaminated environments have rapidly adapted to their presence by evolving new biodegradation pathways that take advantage of them as sources of carbon, nitrogen, and energy. This review provides an overview of the synthesis of both man-made and biogenic nitroaromatic compounds, the bacteria that have been identified to grow on and completely mineralize nitroaromatic compounds, and the pathways that are present in these strains. The possible evolutionary origins of the newly evolved pathways are also discussed. These compounds are organic molecules that consist of at least one nitro group -NO₂ attached to an aromatic ring. The vast majority are synthetic, although several biologically produced nitroaromatic compounds have been identified. The strong electronegativity of the nitro group stems from the combined action of the two electron-deficient oxygen atoms bonded to the partially positive nitrogen atom. This not only provides charge to the molecule but also imparts unique properties that make the nitro group an important functional group in chemical syntheses. The nitro group is strongly deactivating toward electrophilic aromatic substitution of the benzene ring. Both the conjugation state and resonance properties of nitro groups attached to aromatic rings result in partially positive charges at ortho and para positions that act to repel electrophiles, and as a consequence, attacks are directed toward the open meta positions. Furthermore, when aromatic compounds with multiple nitro groups react with electrophiles, stable Meisenheimer complexes can be formed. These characteristics contribute to the stability and recalcitrance to degradation of this class of chemicals. Over the last several years, numerous review articles have specifically addressed the toxicity and mutagenicity of nitroaromatic compounds, the biosynthesis of nitro compounds, and the biodegradation of nitroaromatic compounds. Here we present an integrated review of the chemical and biological syntheses of nitroaromatic compounds and our current understanding of bacterial degradation of these toxic and recalcitrant chemicals. In this fashion, benzene, toluene, and phenol are converted into nitrobenzene, nitrotoluenes, and nitrophenols, the simplest of all nitroaromatic compounds. Conditions can be modified to direct nitration to the ortho, meta, or para position. In the Zincke nitration, phenols or cresols react with sodium nitrite to replace bromines with a nitro group - Nitration can also be tailored to multiple substitutions on a single molecule. The unique chemistry of the nitro group has led to the use of several nitroaromatic compounds in high-energy explosives Fig. As a result, energy is rapidly released from these compounds when an explosive charge is detonated Picric acid 1,3,5-trinitrophenol was first prepared in as a yellow dye for fabrics and has been used in explosive shells. However, the corrosiveness of picric acid, its reactivity with metals to form shock-sensitive salts, and its incomplete detonation led to its eventual disuse. In contrast to picric acid, 2,4,6-trinitrotoluene TNT Fig. Although TNT was widely manufactured by sequential nitration of toluene and was extensively used in both World Wars, it is no longer produced in North America due to problems of environmental contamination and persistence at manufacturing sites. TNT is still found as a major component of many composite explosives

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that include chemicals such as aluminum, barium nitrate, or other explosives, such as the heterocyclic nitroaromatic compounds cyclotrimethylenetrinitramine RDX and cyclotetramethylenetetranitramine HMX ,

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In recent years, research on microbial degradation of explosives and nitroaromatic compounds has increased. Most studies of the microbial metabolism of nitroaromatic compounds have used aerobic microorganisms.