**REDUCTIVE DEHALOGENATION OF
ENVIRONMENTAL CONTAMINANTS:
A CRITICAL REVIEW**

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MANAGEMENT PERSPECTIVE

Many important environmental contaminants are less persistent under reducing conditions such as occur in sediments or flooded soils than under oxidizing conditions. One of the most important of the reductive reactions that occur under these conditions is reductive dehalogenation, i.e., the replacement by a hydrogen atom of a halogen atom (most commonly chlorine, sometimes bromine). The biochemical and microbiological processes involved are discussed in this review.

Pesticides such as DDT and lindane, and solvents such as tetrachloroethylene, are dechlorinated by relatively unspecific reactions, whereas aromatic compounds such as chlorophenols seem to require the presence of specific microorganisms.

It has recently been discovered that many components of polychlorinated biphenyls (PCBs) may undergo reductive dechlorination both in the environment and in the laboratory. Since it is the more highly chlorinated compounds that react most readily in this way, while the less highly chlorinated components are more readily oxidized, it seems possible that a combination of aerobic and anaerobic processes may render these substances less persistent than has been hitherto feared.

PERSPECTIVES DE GESTION

Un grand nombre d'importants contaminants de
l'environnement sont moins persistants en milieu réducteur, comme
celui de sédiments ou de sols inondés, qu'en milieu oxydant.
L'une des principales réductions qui se produit alors est la
déshalogénation, c.-à-d. le remplacement d'un atome d'halogène
(le plus souvent le chlore, parfois le brome) par un atome
d'hydrogène. Les processus biochimiques et microbiologiques
correspondants sont examinés ici.

Des pesticides, comme le DDT et le lindane, et des
solvants, comme le tétrachloréthylène, sont déchlorés par des
réactions relativement communes, alors que des composés
aromatiques, comme les chlorophénols, semblent nécessiter la
présence de micro-organismes spéciaux.

On a récemment découvert que beaucoup de biphényles
polychlorés (BPC) peuvent être déchlorés par réduction aussi bien
dans l'environnement qu'en laboratoire. Etant donné que ce sont
les composés les plus chlorés qui réagissent ainsi le plus
facilement, alors que les composés moins chlorés sont plutôt
oxydés, il semble possible qu'une combinaison de processus
aérobies et anaérobies puisse rendre ces substances moins
persistantes qu'on ne l'a cru jusqu'ici.

ABSTRACT

It is generally recognized that reductive processes are more important than oxidative ones in transforming, degrading and mineralizing many environmental contaminants. One process of particular importance is reductive dehalogenation, i.e., the replacement of a halogen atom (most commonly a chlorine atom) by a hydrogen atom.

A number of different mechanisms are involved in these reactions. Photochemical reactions probably play a role in some instances. Aliphatic compounds such as chloroethanes, partly aliphatic compounds such as DDT, and alicyclic compounds such as hexachlorocyclohexane are readily dechlorinated in the laboratory by reaction with reduced iron porphyrins such as hematin. Many of these are also dechlorinated by cultures of certain microorganisms, probably by the same mechanism. Such compounds, with a few exceptions, have been found to undergo reductive dechlorination of the environment.

Aromatic compounds such as chlorophenols appear not to react with reduced iron porphyrins. Some of these however undergo reductive dechlorination both in the environment and in the laboratory. The reaction is generally associated with methanogenic bacteria. There is evidence for the existence of a number of different dechlorinating enzymes specific for different isomers.

Recently it has been found that many components of polychlorinated biphenyls (PCBs), long considered to be virtually totally resistent to environmental degradation, may reductively dechlorinate both in the laboratory and in nature.

RESUME

Il est généralement admis que les processus de réduction
sont plus importants que ceux d'oxydation lors de la
transformation, de la dégradation et de la minéralisation de
nombreux contaminants de l'environnement. Une réduction
particulièrement importante est la déshalogénation, c'est-à-dire
le remplacement d'un atome d'halogène (le plus souvent un atome
de chlore) par un atome d'hydrogène.

Différents mécanismes interviennent dans ces réactions.
Il peut y avoir parfois des réactions photochimiques. Des
composés aliphatiques, comme le DDT, et des composés
alicycliques, comme l'hexachlorocyclohexane, sont facilement
déchlorés en laboratoire par réaction avec des porphyrines de fer
réduites, telle l'hématine. Beaucoup de ces produits sont
également déchlorés par les cultures de certains micro-
organismes, probablement par le même mécanisme. A quelques
exceptions près, on a observé que ces mêmes produits subissaient
une déchloration réductrice dans l'environnement.

Les composés aromatiques, comme les chlorophénols, ne
semblent pas réagir avec les porphyrines de fer réduites.
Cependant, certains d'entre-eux sont réduits par déchloration
aussi bien dans l'environnement qu'en laboratoire. La réaction
est généralement associée à des bactéries méthanogènes. On a pu

constater qu'il existait différentes enzymes de déchloration, spécifiques pour différents isomères.

Récemment on a observé que beaucoup de biphényles polychlorés (BPC), longtemps considérés comme totalement réfractaires à la dégradation environnementale, pouvaient être réduits par déchloration aussi bien en laboratoire que dans la nature.

INTRODUCTION

When the presence of man-made chemicals in the environment first became a matter of concern and the pathways of their microbial degradation consequently became a matter of interest, attention was initially focused on oxidative, aerobic processes. This was perhaps because biochemists were more familiar with oxidative processes than with reductive ones, the techniques were probably easier, and oxidative processes offered at least a possibility of complete degradation. Many of the compounds of greatest concern proved very resistant to oxidative degradation.

However, in 1967 Hill and McCarty (1) reported that a number of these compounds more or less readily underwent at least primary degradation under reducing conditions in sewage sludge. At about the same time studies with flooded soils, particularly flooded rice paddies, showed that many of these compounds were rapidly transformed in these environments (2,3,4).

Among the various types of reductive reactions that may occur, reductive dehalogenation, the replacement of a halogen atom by a hydrogen atom, is of particular interest. The purpose of this review is to summarize existing knowledge of reactions of this type and to attempt to assess their importance in the transformation of contaminants in the environment. The task has been made easier by the existence of two recent reviews (4,5) which have surveyed much of the earlier literature from somewhat different viewpoints.

## REDUCTIVE DECHLORINATION OF ALKYL HALIDES

Chlorinated Pesticides

DDT was one of the first organochlorine insecticides to come into general use and it continued to be used for many years, often on a very large scale, because of its effectiveness, cheapness, and low mammalian toxicity (4,5). Ultimately, recognition of its extreme persistence led to severe curtailment of its use. It is not totally resistant to chemical transformation in nature, and undergoes dehydrochlorination to DDE and reductive dechlorination to DDD. DDE formation is an enzymatic reaction, catalyzed by specific dehydrochlorinases found in many organisms (8). DDD formation has been reported in a variety of systems: in actively fermenting yeast (9); in the tissues of dead animals (10); in frozen blood (11); and in cultures of various microorganisms such as Aerobacter aerogenes (12). In this organism it was established that the reductive dechlorination occurs directly, not by dehydrochlorination to DDE and subsequent reduction, because DDT labelled with deuterium in position 2 gave rise to DDD still containing the isotope (13). Both intact cells and cell-free extracts of this organism brought about further dechlorination and degradation of DDD (14).

In general it appeared that the dechlorination of DDT was not catalyzed by a specific enzyme but merely required reducing conditions in the presence of any of a variety of biological materials. An explanation of the reaction was provided by investigations carried out

around the same time on the reaction between a variety of alkyl halides and reduced iron porphyrins, in which the iron is oxidized and the alkyl halide reductively dechlorinated (15). The initial step appears to be a reaction between the alkyl halide and the iron (II) atom of the prophyrin to yield a halide ion, iron (III) porphyrin, and an alkyl free radical:

$$RX + Porphyrin - Fe^{++} \rightarrow R\cdot + X^- + Porphyrin - Fe^{+++}$$
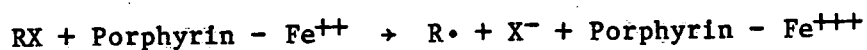
The free radical is converted to an alkane by reaction with a proton and a second iron (II) atom:

$$R\cdot + H^+ + Porphyrin - Fe^{++} \rightarrow RH + Porphyrin - Fe^{+++}$$
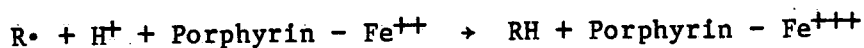
or in some other way (16).

Not only free iron porphyrins but also a number of heme proteins are capable of reacting in this fashion (17). Similar compounds containing cobalt, such as vitamin B_{12}, may also take part in reactions of this kind (18).

Reduction of DDT in sewage sludge produces DDD (1,19,20). The rate is increased by the addition of a suitable reducing agent such as sodium dithionite, and the activity of the sludge is not diminished by autoclaving (20). Rapid reduction of DDT to DDD was found to occur in a mixture of hematin, a reducing agent (sodium dithionite or ferrous

sulphate) and an emulsifying agent or ethanol to prevent precipitation of the reduced hematin (20). A variety of products other than DDD may also be formed (21,22) perhaps by other reactions of the initially formed free radical, or by subsequent reactions of DDD. It is clear, therefore, that hematin can act under reducing conditions as a catalyst for the reductive dechlorination of DDT, and it seems likely that many, if not all, of the reported instances of this reaction can be attributed to this process.

Many other chlorinated insecticides and some of their transformation products have been shown to undergo some degree of transformation under reducing conditions, although in many instances no products have been identified, or even detected. Thus it is not possible to decide whether they have been dechlorinated or changed in some other way. In sewage sludge the rates of degradation were approximately lindane > heptachlor > endrin > DDT > DDD > aldrin > heptachlor epoxide > dieldrin (1). The rate of degradation of the last two was very low. In one study of flooded tropical soils (23) DDT, DDD, methoxychlor and heptachlor were degraded fairly quickly, while endrin, aldrin, chlordane and dieldrin were more persistent. In flooded soils in the temperate zone, heptachlor, DDT, lindane and endrin were degraded at rates decreasing in that order, while dieldrin and DDT were relatively persistent (23).

Several insecticides have been studied more intensively. After DDT, lindane has probably received the most attention. Lindane is the

γ-isomer of 1,2,3,4,5,6-hexachlorocyclohexane (HCH). It is the only one of the various isomers that is strongly insecticidal (25). It is used either as the pure isomer or as a technical mixture of several isomers referred to as benzenehexachloride (BHC). In flooded rice field soil it was found to undergo reductive dechlorination to γ-3,4,5,6-tetrachlorocyclohexene (γ-BTC) which then underwent further degradation (25).

Some of the non-insecticidal isomers proved much more persistant than the γ-isomer under field conditions in Japanese soils (4). Similar differences were found with soil suspensions of some soils (27) but not of others (28).

A pure culture of a species of _Clostridium_ was found to convert lindane to an unidentified product which was not γ-pentachlorocyclohexene (29). Subsequent studies with the same organism, identified as _Clostridium_ _sphenoides_, showed that it degraded both α- and γ-HCH to tetrachlorocyclohexenes, which were further degraded to unknown products (30).

A survey of a number of facultative and obligate anaerobic organisms found that several of these could dechlorinate hexachlorocyclohexane isomers under reducing conditions (31). With all species, the α-, β-, and δ-isomers were degraded more slowly than the γ-isomer. The principal intermediate detected was γ-tetrachlorocyclohexene. Some strains were able to convert virtually all the chlorine in ^{36}Cl-labelled γ-HCH to chloride ions in a few days.

Another survey of a number of species of Clostridium revealed that several could degrade γ-HCH and two could degrade α-HCH, but none could attack the β- and δ-isomers (32). Suspension and cell-free extracts of one species, isolated from paddy soil, degraded γ-HCH forming γ-tetrachlorocyclohexene and traces of monochlorobenzene (33). ^{14}C-labelled γ-HCH disappeared in a few weeks for samples of flooded alluvial soil. Very little could be accounted for either as [14]CO_2 or as soil-bound residue, suggesting that volatile products other than CO_2 were formed (34e).

Methoxychlor is similar in structure to DDT and might perhaps be expected to undergo similar reactions. It was degraded to unknown products by the Clostridium species that degraded lindane (2). Radioactive methoxychlor underwent primary degradation in soil under anoxic conditions but little or none of the radioactivity appeared in volatile products. After several months of incubation under anoxic conditions, radioactivity appeared in CO_2 when the mixture was exposed to air, suggesting that reductive processes give rise to products more susceptible to oxidation than the original compounds (35).

Mirex is one of the most persistent of the chlorinated hydrocarbon pesticides (36). It is, however, readily dechlorinated by reduced hematin (37). The nature of the products depends on the molar ratio of hematin to mirex. At a ratio of 5:1 a number of products were identified in which one or two chlorine atoms had been replaced

by hydrogen, while at a ratio of 10:1 further reactions appear to have occurred leading to products not detectable by gas chromatography.

Toxaphene is a mixture of a large number of chlorobornanes obtained by chlorination of camphene(8,25). It has been shown to disappear from soil, particularly under anoxic conditions (38,39). Several of the components of toxaphene can be reductively dechlorinated by reduced hematin (40,41).

Alochlor was shown to undergo reductive dechlorination in an anoxic stream sediment (42).

It is evident from the foregoing survey that transformation of chlorinated pesticides is not uncommon. In some instances there is convincing evidence that reductive dechlorination occurs. Reaction with a reduced iron porphyrin is certainly one mechanism for this and there is little evidence for the existence of any others. In many experiments with such materials as soils and sewage sludge the rate of the reaction has been shown to be greatly reduced by prior autoclaving or poisoning with antiseptics, and this has been taken as evidence that biological processes are involved. However, it does not necessarily follow from this the process is a truly biochemical one, in the sense of being enzymatically catalyzed. Bacteria may serve merely to maintain reducing conditions so that hematin may serve as a catalyst. In experiments with bacterial cultures or suspensions it still cannot be assumed that the reaction is an enzymatic one, and

not a spontaneous reaction with metal porphyrins in the cells, maintained in a reduced state by the organisms' metabolic activity.

There is a little evidence that photochemical processes, either direct or sensitized, may cause reductive dechlorination of some compounds under certain conditions. The photodecomposition of permethrin was shown to yield reductively dechlorinated products in very small amounts, along with much larger amounts of products produced by other types of reactions (43). The superoxide ion, O_2^-, was reported to reductively dechlorinate a number of cyclodiene insecticides (44). Superoxide can be produced photochemically both in fresh water (45) and in sea water (46) so it is at least conceivable that this reaction may be environmentally significant under certain conditions.

Halogenated Alkanes and Alkenes

Severe restrictions on the use of the more persistent organochlorine insecticides have made the investigation of their fates a matter of less pressing concern. In recent years, however, another class of organohalogen compounds, halogenated (especially chlorinated) hydrocarbons with one or two carbon atoms, have been found to be very widely distributed in ground waters (47). These compounds are chiefly used as solvents, although some have been used as pesticides.

There is evidence that some of these, too, are susceptible to reductive dehalogenation. It was shown 20 years ago that ethylene dibromide, 1,2-dibromo-3-chloropropane, and 2,3-dibromobutane, all

compounds used as nematocides, are reductively dehalogenated in soil cultures (48). It was later shown (49) that several trihalomethanes were degraded in growing mixed methanogenic cultures. Subsequent studies showed that chlorinated 2-carbon compounds could also react in this way (50). 1,1,2,2-tetrachloroethane and tetrachloroethylene were almost completely degraded to CO_2; under some conditions 1,1,2-trichloroethane and trichloroethylene were detected suggesting that the first step was probably a reductive dechlorination. Ethylene dibromide was also dehalogenated, probably to ethylene, under similar conditions (51). These reactions were almost certainly due to methanogenic organisms and not to other organisms present in the mixed cultures, because pure cultures of several methanogens have been shown to dehalogenate several bromo and chloro compounds to the corresponding hydrocarbons (52).

Both cis- and trans-1,2-dichloroethylene were found in well water where groundwater was contaminated with trichloroethylene, and both isomers as well as vinyl chloride were apparently formed in experiments using muck from the aquifer (53).

Trichloroethylene was converted to 1,2-dichloroethylene, but not to 1,1-dichloroethylene, in experiments using soil from a site contaminated by a spill of trichloroethylene (54). In microcosms prepared from uncontaminated Florida muck, similar reactions were observed (55). In other experiments, microcosms prepared using sandy organic sediment previously contaminated with trichloroethylene

converted added TCE to cis-1,2-dichloroethylene in a year, whereas in microcosms prepared from crushed rock and water containing few bacteria, TCE disappeared but little dichloroethylene was formed (56). Chlorinated alkanes reacted more rapidly than chlorinated alkenes. Tetrachloroethylene can be dechlorinated, presumably stepwise, to vinyl chloride (57,58). This compound has also been observed as a reduction produce of dichloro- and trichloroethylene (59).

Hexachloroethane can be converted to tetrachloroethylene (60).

Some chlorinated methanes and chlorinated ethanes are dechlorinated by reduced hematin (61). Carbon tetrachloride, chloroform, and 1,1,1-trichloroethane were reduced, while methylene chloride, 1,1,2-trichloroethane, and 1,1-dichloroethane were not. 1,1,2,2-tetra-chloroethane underwent dehydrochlorination rather than reductive dechlorination and the reaction did not require hematin. Tri- and tetrachloroethylene did not react. It seems possible that reactions other than that with hematin, perhaps enzymatic ones, are responsible for the observed degradation of these compounds.

Cytochrome P-450 is involved in the metabolism of foreign substances in a wide range of organisms from bacteria to mammals. Most commonly it is the oxidized form (Fe^{III}), that is active, causing oxidative transformation or degradation of the substrate. It has recently been shown, however, that the reduced (Fe^{II}) form of bacterial cytochrome P-450 can cause the reductive dehalogenation of a

variety of substances, presumably by the same mechanisms as hematin.
Reduction can be brought about by purified cytochrome or by cytochrome
in intact cells. Compounds reduced include chloropicrin (trichloro-
nitromethane) (62), mono- and dichloronitromethane, carbon tetra-
chloride and bromotrichloromethane (63) and 1,2-dibromo-3-chloropro-
pane (64).

REDUCTIVE DECHLORINATION OF ARYL HALIDES

The studies on flooded rice fields referred to earlier seem to
have provided the first evidence that aryl chlorides, like alkyl
chlorides, may undergo reductive dechlorination (4,65,66). Some of
the reactions were of great importance. Thus 2,3,4,5,6-pentachloro-
benzyl alcohol, used as a fungicide, was degraded to the corresponding
pentachlorobenzoic acid which in turn was partially dechlorinated to
tetrachlorobenzoic acid. These compounds are strongly phytotoxic and
caused serious damage to crops (67). Another fungicide, 4,5,6,7-
tetrachlorophthalide, was converted to 4,6,7-trichloro- and 4,6- and
4,7-dichlorophthalide among other products. None of these was phyto-
toxic (68). A related compound, techlofthalam, has also been shown to
undergo reductive dechlorination of the tetrachlorophthalamic acid
moiety (69).

Several herbicides of various types have been found to undergo
reductive dechlorination. Thiobencarb, used in Asian rice fields, was

converted in highly reducing soils to S-benzyl-N,N-diethylthiocarba-
mate, which proved toxic to rice (70). Chlornitrofen undergoes reduc-
tion in rice paddy soils (71) and diuron reduction was observed in
pond sediments (72).

2,4,5-trichlorophenoxyacetic acid (2,4,5-T) was dechlorinated at
the para position (73) by a consortium of anaerobic methanogenic
bacteria that had previously been shown to dechlorinate several mono-
and dihalobenzoic acids (74).

The reductive dechlorination of halobenzoic acids seems probably
to be enzymatic. In anaerobic organisms it is inhibited by oxygen and
displays a certain degree of specificity with respect to the positions
of the halogen atoms on the aromatic ring (74). Sediments require a
period of acclimation to halobenzoates, but once acclimation has
occurred further dehalogenation proceeds without a lag (75). The pro-
cess follows Michaelis-Menten kinetics, and substrates can apparently
compete with one another (76). An organism with the ability to
dechlorinate 3-chlorobenzoic acid was isolated from the consortium
(77).

The capacity to bring about reductive dechlorination is not
limited to anaerobic organisms. A strain of Alkaligenes denitrificans
was shown to reduce 2,4-dichlorobenzoate to 4-chlorobenzoate as one
step in an overall oxidative sequence (78).

Chlorophenols are important industrial chemicals both as final
products used as biocides and as intermediates in the manufacture of

such products as 2,4-D and 2,4,5-T. They may also be formed inciden-
tally in the course of such industrial processes as the bleaching of
wood pulp (79,80) and possibly also when wood is burned as fuel, or in
forest fires (79). They appear to undergo reductive chlorination in
ways similar to the halobenzoic acids. Fresh sewage sludge was found
to dechlorinate monochlorophenols, the rates of disappearance of the
various isomers being in the order 2->3->4- (81d). Sludge could be
acclimated to a variety of monochlorophenols (82). At least two
distinct microbial activities were demonstrated, one dechlorinating in
the ortho and para positions, the others in the meta and para posi-
tions. The relative rates of reaction of the three isomers was the
same as with fresh sludge. Monochlorophenols could be detected as
intermediates in the degradation of dichlorophenols.

Anaerobic cultures prepared from sludge from a different source
dechlorinated 2-chlorophenol rapidly, but the other isomers were
attacked much more slowly. In contrast to the prevous results, the
3-isomer was a little more resistant than the 4-isomer (83).

In other experiments, 2,4,5-T was converted through 2,4,5-tri-
chlorophenol and 4,5-dichlorophenol to 4-chlorophenol. 2,4,6-tri-
chlorophenol was also converted to 4-chlorophenol. In these experi-
ments the 4-chlorophenol persisted. With 2,4-D, however, 4-chloro-
phenol was formed but subsequently disappeared. With pentachloro-
phenol, ortho dechlorination led to 3,4,5-trichlorophenol which unlike

other trichlorophenols tested underwent para dechlorination to 3,5-dichlorophenol, which persisted (84).

Several mono- and dichlorophenols were dechlorinated in microcosms prepared from methanogenic, but not from non-methanogenic, aquifer material (85). Several chlorobenzoic acids behaved similarly (86).

Soil and sediments from a variety of sources were found to dechlorinate a number of chlorophenols. The relative ease of removal of substituents from various positions was ortho   para   meta (90).

Pentachlorophenol has been used as a herbicide and on a much larger scale as a wood preservative. Consequently, it has become a widely distributed environmental contaminant. In flooded rice field soil it was found to undergo dechlorination at the ortho, meta or para position yielding all three of the possible tetrachlorophenals. Further degradation of these led to at least four trichlorophenols (87). Some dechlorination at the meta and para positions occurred in sterilized soils, presumably by non-biological processes (88).

A mixture of three sewage sludges, acclimated to 2-, 3- and 4-chlorophenol, respectively, mineralized pentachlorophenol to carbon dioxide, methane, and chloride ion (89).

Chlorobiphenyls are widely distributed in the environment. They were formerly produced industrially in large quantities as complex mixtures known as polychlorinated biphenyls (PCBs) by chlorination of biphenyl. Although their use has been greatly curtailed in recent

years, some congeners are among the most persistent environmental contaminants (91).

In an early study (92) a PCB mixture in fermenting silage showed no change in the proportions of its components after many months. It seemed unlikely that all the components would have been degraded at exactly the same rate, so it was concluded that no dechlorination had occurred. Relative depletion of certain components with depth was found in sediment cores from a coastal marine environment, but it was the less highly chlorinated congeners that were depleted, suggesting that the depletion was unlikely to have been due to reduction (93) because it is the more highly chlorinated compounds that would be most easily reduced (94).

However, analysis of sediment cores from the upper Hudson River showed relative depletion of the more highly chlorinated congeners in the lower layers, strongly suggesting that reductive dechlorination had occurred at this site (96). More extensive studies with samples from a variety of sites led to the conclusion that a number of distinct processes are involved, with specificities with respect to substitution positions and molecular shape (96,97).

Aryl chlorides, like alkyl chlorides, may undergo photochemical reduction. Irradiation of chlorobenzoic acids (98) and of chloro-phenylacetic acids (99) yields benzoic acid and phenylacetic acid, respectively, among other products. Photolysis of pentachlorophenol yielded tetra- and trichlorophenol among the products (100).

Chlorobiphenyls (101,102,103) and bromobiphenyls (104,105) may also undergo photoreduction to less highly halogenated products (101,102).

Certain inorganic metal compounds present in natural waters may serve as photocatalysts for a variety of reactions including reductive dechlorination. The superoxide ion may be involved in some of these (106). These processes may ultimately prove to be of importance not only in the degradation fo contaminants in the environment, but also in their removal from waste waters under controlled conditions.

DISCUSSION AND CONCLUSIONS

Reductive dechlorination under environmental conditions is by no means a rare phenomenon. Indeed with many compounds, especially highly chlorinated ones, it probably represents a more important pathway of transformation and degradation than oxidative processes do.

It is clear that a number of mechanisms are involved. With chlorinated insecticides the reaction with reduced hematin is likely the most important, and for many compounds it may be the only one that plays a significant part. This reaction is also involved in some reductive dechlorinations of chloroalkanes. However, not all the compounds of this class that undergo dechlorination in the environment appear to be capable of reacting with hematin; the reaction seems to be limited to compounds with three or four chlorine atoms on the same carbon atom (61).

Although there is not much evidence one way or the other at the present time, it seems possible that some alkanes may be dechlorinated by anaerobic bacteria. There is convincing evidence that this is one, and probably the most important, pathway for the anaerobic degradation of chlorophenyl acids and chlorophenols. The organisms involved are probably methanogens and suitable organisms, or consortia of organisms, can bring about the total mineralization even of such recalcitrant compounds as pentachlorophenol. A number of dechlorinating enzyme systems appear to exist of differing specificty, which either occur in distinct organisms or can be independently induced.

The suggestion that chlorobiphenyls may be reductively dechlorinated is of particular interest. If this can be confirmed it will allow a radical reassessment of present views on the persistence of these troublesome contaminants.

The possibility of anaerobic mineralization of aryl chlorides as a means of purifying effluents is attractive (107). On theoretical grounds, reductive processes might be expected to be favoured over oxidative ones, since chlorination decreases the electron density of the aryl ring making attack by electrophilic reagents, such as oxygen, more difficult. Moreover, the partial aerobic degradation of many chlorophenols (108) and some chlorobiphenyls (109) yields products which can undergo autoxidation to dark polymeric material that is extremely persistent.

Photoreductive dechlorination of many organochlorine compounds is thermodynamically and kinetically possible, although quantitatively it may be of relatively minor significance in natural conditions except perhaps with relatively water-soluble compounds, since others are unlikely to remain long in well-lighted areas before being buried in soils and sediments. It may be of considerably more significance in effluents under controlled conditions.

The likely importance of photoreductive processes in converting recalcitrant compounds into substances more susceptible to biochemical attack has been stressed (106). More generally, alternation between reducing and oxidizing conditions may lead to more extensive degradation than can occur under constant conditions; this seems to be true of methoxychlor (35). Conversely, the commonest environmental transformation product of heptachlor, heptachlor epoxide, seems more resistent to dechlorination than the parent compound. Here, prior exposure to oxidative conditions renders the compound less susceptible to reductive attack.

The significance of reductive dechlorination, like that of any aspect of environmental chemistry, can only be assessed in the context of the wide range of biochemical, photochemical and other types of transformations all proceeding simultaneously or successively in that exceeding complex reactor, the biosphere.

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