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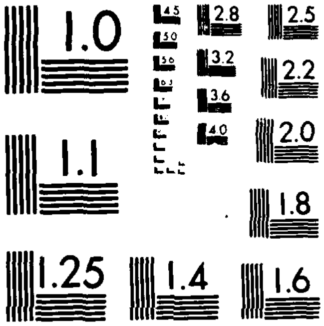

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Kinetics and Degradation Products of Trichloroethene

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Existing literature was reviewed to identify proposed or demonstrated instances of degradation of trichloroethene (trichloroethylene or TCE) by biological or abiotic mechanisms. The information was evaluated for possible future research into abiotic degradation mechanisms, thereby, increasing our understading of in situ processes occuring in TCE-contaminated sites providing alternate treatment technologies.

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PREFACE

This report was prepared for the Air Force Engineering and Services Center, Engineering and Services Laboratory, Tyndall AFB Florida, under Job Order Number (JON) 1900 2074. Captain Jack H. Jeter was the AFESC/RDVW project officer.

This report was completed at the University of Florida, Gainesville, by personnel from the Department of Environmental Engineering Sciences. All efforts were conducted under Task Order Contract (TOC) Number F08635-83-C-0136 T.O. 85-5.

This report has been reviewed by the Public Affairs Office (AFESC/PA) is and releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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KINETICS AND DEGRADATION PRODUCTS
OF TRICHLOROETHENE

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SECTION I

INTRODUCTION

A. OBJECTIVE

The literature was reviewed to identify proposed or demonstrated instances of degradation of trichloroethene (trichloroethylene, or TCE) by biological or abiotic mechanisms. The information was evaluated for possible future research into abiotic degradation mechanisms, thereby, increasing our understanding of in situ processes occurring in TCE-contaminated sites or providing alternate treatment technologies.

B. *BACKGROUND*

Trichloroethene is a widely used priority pollutant. Numerous instances of groundwater contamination by TCE have been documented. These have been explained by TCEs high mobility and relative resistance to degradation.

The standard approach to evaluating transformation of chemicals in the environment has been to examine reactivity with common components such as water or oxygen; photochemical processes; and biodegradation. Other chemical reactions (addition, substitution, and elimination) are considered to be rare (References 1 and 2). Much of the information available on priority pollutant degradation has emphasized air and aquatic environments. The emphasis in this report was placed on possible abiotic reactions in the vadose zone and in groundwater, because of concern over behavior of TCE as a contaminant in those media.

As a common pollutant, considerable attention has been paid to TCE's physical and chemical properties which are expected to play a dominant role in its environmental fate. These properties include volatility, biodegradability, and susceptibility to photolysis and hydrolysis. In 1979, the U.S. Environmental Protection Agency (EPA) reported that volatilization, followed by photooxidation in the troposphere, was the primary mode for removal of TCE from aquatic environments. Trichloroethene was reported as resistant to hydrolysis and "no information was found indicating that microorganisms exist which can readily degrade trichloroethene" (Reference 3).

Since that time, biological oxidation and reduction have been demonstrated in the laboratory (References 4 and 5). Reduction products include vinyl chloride and isomers of dichloroethene which are also priority pollutants. These have been detected during contamination investigations on sites where the products were not, in themselves, used (Reference 6). Oxidation degradation products are not typically measured during contamination investigations; thus, the contribution of oxidation to the loss of TCE in soils and groundwater is unknown.

The role of abiotic degradation in soils and groundwater has not been extensively studied and in some cases it is difficult to clearly establish the role of chemical versus biological degradation mechanisms (Reference 7). The presence of surfaces which can catalyze reactions, form complexes, or provide localized microenvironments of variable pH or redox require a reexamination of the importance of abiotic degradation of pollutants in these subsurface environments.

The mechanisms, reaction conditions, and kinetics of chemical reactions of TCE were reviewed and this information interfaced with available information on conditions in the vadose zone or groundwater environments.

C. PROJECT APPROACH/SCOPE

The literature sited in this report was selected on the basis of information obtained from on-line computer searches, library research, and texts on environmental and organic chemistry. The search strategy for the chemistry of TCE compiled sources addressing kinetics and mechanisms of oxidation-reduction, elimination, addition and substitution reactions.

References on environmental behavior include information on transport, photolysis, biodegradation, and hydrolysis. Since the emphasis of this study was primarily on degradation processes in the subsurface, references on transport and photolysis were not comprehensively reviewed.

An effort was made to avoid redundant coverage of topics which have been widely studied and cross-referenced. Articles and abstracts were generally restricted to those in English, although a variety of foreign journals were included in the original literature searches.

The goals varied for the research studies reviewed. These included documenting reactions of economic importance for industrial processes, safety and toxicity evaluations, obtaining maximum yields for an organic synthesis reaction, and examining effects of radiation. Some of the information could not be directly evaluated for environmental applicability due to the different objectives affecting the experimental designs. Selected reactions cited in the literature required additional review of methods, reactants, and mechanisms; some of these were discussed with Dr. M. Battiste in the Department of Chemistry at the University of Florida. Characteristics of the subsurface which may promote a particular reaction were also discussed with Dr. P.S.C. Rao of the Soil Science Department.

Questions developed during review of the literature. A variety of research recommendations required different levels of effort (time and money) and must be evaluated in relation to the goals and interests of the Air Force. Selected key questions were identified to increase understanding and evaluate potential treatment of contaminated soil and groundwater.

SECTION II

TCE: OVERVIEW OF STRUCTURE AND REACTIVITY

A. STRUCTURE AND PROPERTIES

Trichloroethene is a halogenated alkene. The structure and physical properties of TCE (Reference 8) are summarized in Table 1. Degradation of TCE may occur by attack of the carbon-carbon double bond, carbon-chlorine bonds or carbon-hydrogen bond.

The approximate bond energies for various bond types are:

Approximate Bond Energies (Reference 9)

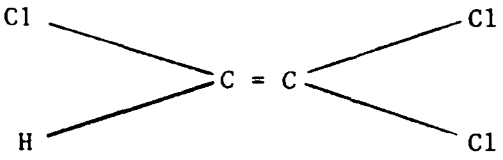
	kcal/mole
C-H	96-99
C-C	83-85
C-Cl	79
C=C	146-151

The properties of TCE can be compared to other simple halogenated olefins which may be detected in sites where TCE has been disposed. Thermodynamic data for these compounds are summarized in Table 2 (Reference 10), while the molecular properties summarized by Skinner and Rabinovitch (Reference 11) are given in Table 3.

B. REACTIVITY OF THE CARBON-HYDROGEN BOND

The electron-withdrawing effect of the chlorine atoms in TCE increases the acidity of the single hydrogen atom:

TABLE 1. SOME PROPERTIES OF TRICHLOROETHENE.[a] (REFERENCE 8)

Structural formula:	
Molecular weight:	131.40
Boiling range:	87.14 - 87.55°C (Solidifies at -83°C)
Specific gravity:	1.465 at 20.4°C
Vapor pressure:	60 mm Hg at 20°C
Solubility:	Soluble in ether, alcohol, chloroform Solubility in water: 0.1 g/100 g water at 25°C
Distribution coefficient:	Water/air: 3 at 20°C Fat/water: 34.4

[a] Adapted from Aviado et al., 1976

TABLE 2. THERMODYNAMIC DATA OF TCE AND RELATED OLEFINS (REFERENCE 10)

	TCE	Ethylene	Vinyl chloride	1,1-DCE	cis-1,2-DCE	trans-1,2-DCE	Tetrachloroethene
$H^{\circ}_{f(300)}$							
Kcal mol^{-1}	-2.0	12.5	8.6	4.3	1.0	1.2	-2.7
KJ mol^{-1}	-8.4	52.3	36.0	18.0	4.2	5.0	-11.3
$S^{\circ}_{(300)}$							
cal $mol^{-1}K^{-1}$	77.5	52.4	63.0	69.7	70.8	70.8	81.3
J $mol^{-1}K^{-1}$	324.3	219.4	263.6	291.7	296.5	296.5	340.4
$Cp^{\circ}_{(300)}$							
cal $mol^{-1}K^{-1}$	19.3	10.3	13.0	16.5	15.8	15.8	22.8
J $mol^{-1}K^{-1}$	80.8	43.1	54.4	69.0	66.2	66.2	95.5

TABLE 3. MOLECULAR PROPERTIES OF ETHYLENES (REFERENCE 11)

	C_2H_4	C_2H_3Cl	$C_2H_2Cl_2$			C_2HCl_3	C_2Cl_4
			cis	trans	asym		
Molecular Weight	28.0	62.5	97.0	97.0	97.0	131.4	165.8
Moments of Inertia							
$I_A \times 10^{38}$ g cm^2	0.0575	0.149	0.73	0.153	1.12	7.6	5.9
$I_B \times 10^{38}$ g cm^2	.280	1.40	3.30	6.42	2.46	5.4	4.4
$I_C \times 10^{38}$ g cm^2	.338	1.55	4.03	6.59	3.59	2.1	10.3
Vibrational Frequencies, cm^{-1}							
C=C stretch	1623	1614	1587	1578	1616	1587	1571
torsion	1027	947	406	227	686	211	110
stretch	3272	3129	3077	3088	3130	3085	1000
	3105	3090	3072	3073	3035	932	908
	3019	3040	848	846	788	840	777
	2990	718	711	817	601	628	447
bends	1444	1377	1294	1274	1391	1245	512
	1342	1281	1179	1200	1088	780	347
	1236	1039	876	895	874	450	312
	949	902	697	763	458	381	285
	943	615	571	350	375	274	235
	810	395	173	250	299	172	175

Basic solutions, particularly in polar solvents such as water, favor the formation of the ionic species. The intermediate carbanion shows greater reactivity than nonpolar TCE molecule. Rearrangement results in formation of dichloroacetylene, an elimination product. The enhanced acidity of the hydrogen is used to advantage in synthesis reactions which are typically performed under basic condition.

This property is important in many non-free-radical reactions of TCE. The wide variety of implications of this reaction will be addressed in Section III.

C. NATURE OF THE CARBON-HALOGEN BOND

The bond length for a vinyl C-Cl bond is 1.73 A, as compared to 1.78 A for a saturated C-Cl bond, which implies a stronger bond for chlorine atoms associated with the unsaturated carbon system. The relative inertness of vinyl chloride to nucleophilic substitutions is ascribed to the partial double-bond character of the carbon-halogen bond, making the bond cleavage more difficult (Reference 12).

Reactions of TCE which result in a substitution of a nucleophile for a chlorine atom have been documented. The proposed mechanism is a base-catalyzed "elimination-addition" rather than the more common S_N1 or S_N2 mechanisms. The documented reactions occur under basic conditions in which the carbanion forms. The neighboring negative charge helps in the carbon-halogen bond cleavage (Reference 13). The reaction is base-catalyzed and is discussed in greater detail in Section III.

Cleavage of the carbon-halogen bond also occurs upon reaction with metal hydrides, which results in substitution of a hydrogen for the chlorine atom. Mechanisms for these reduction reactions are much less well-defined and may involve free radicals.

D. ATTACK AT THE CARBON-CARBON DOUBLE BOND

One of the most characteristic reactions of unsaturated molecules is addition, in which reacting atoms or compounds saturate the multiple bond. This can occur by free radical, ionic or heterolytic mechanisms. Trichloroethene is susceptible to attack by free radicals, which act by addition to the double bond. This is discussed in Section IV.

Electrons in a carbon-carbon double bond are considered to be more exposed than electrons in a single bond. These electrons are characteristically susceptible to attack by electrophilic agents (Reference 12). Electron-donating groups (eg. CH3-) increase the reactivity of a double bond toward electrophilic addition.

Chlorine is an electron-withdrawing group, thus, electrophilic substitution reactions involving TCE are inhibited because the chlorine atoms reduce the electron density of the double bond.

These "electron-deficient double bonds" are more susceptible to nucleophilic attack. The effect of substituents is great and according to March (Reference 9) "simple olefins do not react by the nucleophilic mechanism whereas polyhalo-olefins do not react by the electrophilic mechanism."

Whereas ethylene reacts by electrophilic addition to the double bond, susbstitution competes with addition for the polyhalogenated olefins. The reactions of the chlorinated olefins occur by addition-elimination or elimination-addition. The products of these reactions are apparent substitution reactions.

General discussions of the behavior of these simple olefins imply that TCE may react, under non-free-radical conditions, by simple nucleophilic addition. Specific examples of this were not found because reactions were typically conducted under conditions of elevated temperatures and/or use of strong base. These conditions favor formation of an olefin rather than the saturated compound. Evidence of nucleophilic addition under milder conditions was not found.

SECTION III

ELIMINATION AND BASE CATALYZED REACTIONS

A. ELIMINATION

The overall elimination reaction of TCE is shown in Figure 1. This is a dehydrochlorination reaction which generates dichloroacetylene (DCA) and hydrogen chloride. This reaction has been documented for a number of years since TCE reacts quickly and spontaneously with alkali metal hydroxides.

Kim and Choo (Reference 14) examined the thermal decomposition of TCE at 440-460 C/10-900 torr to form DCA and HCl. The Arrhenius parameters were: log A = 13.8 s^{-1} and E = 56.6 kcal/mol.

Molecular elimination reactions have also been induced by infrared laser reaction (Reference 15), in the presence of epoxides and ionic halides (Reference 16), and pyrolysis (Reference 17).

Mechanisms of elimination reactions refer to the movement of the atoms (nuclei) in their rerrangement from the initial to the final state, and especially to the configuration of the transition state. The following three modes (E1, E2, and ElcB) are usually distinguished by their timing in the formation of the intermediates:

E1: $X\text{-}C\text{-}C\text{-}H \text{ -----> } X^{-} + {}^{+}C\text{-}C\text{-}H \text{ -----> } C{=}C + HX$

E2: $X\text{-}C\text{-}C\text{-}C \text{ -----> } X_{8-}\text{-}C\text{-}C\text{-}_{8+}H \text{ -----> } C{=}C + HX$

ElcB: $X\text{-}C\text{-}C\text{-}H \text{ -----> } X\text{-}C\text{-}C^{-} + H^{+} \text{ -----> } C{=}C + HX$

The ElcB (cB = conjugated base) is a carbanion mechanism which occurs in two steps. It is a second-order mechanism and has been

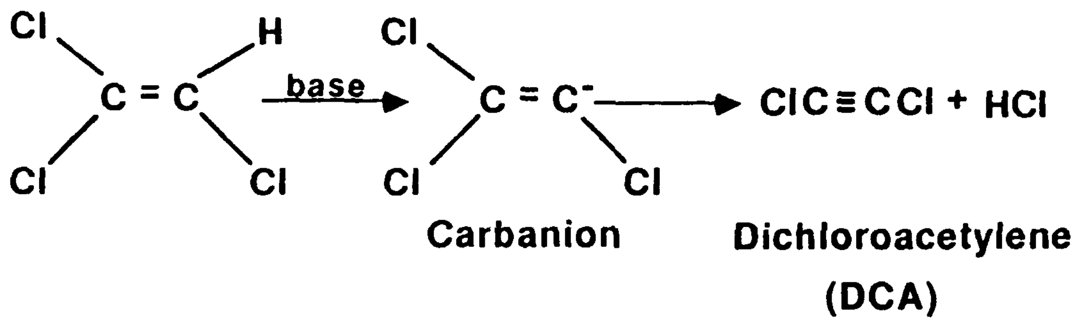


Figure 1. Base Catalyzed Elimination of TCE

implicated as the probable mechanism for the documented elimination reaction of TCE. The electron withdrawing effect of the chlorine atoms increases the acidity of the hydrogen, promoting the formation of the carbanion. The first step in this reaction is an acid-base reaction.

There is controversy over the occurrence of the ElcB mechanism and it may be better considered to be a modification of the E2 mode. In the E2 mechanism, also called the concerted or multicenter process, the hydrogen and halogen are extracted in one step. The transition state may not be fully synchronous and the reaction will normally begin with the lengthening of only one bond. This mechanism covers a broad range of possibilities with tendencies toward El or ElcB. Even the extremes should not be regarded as clearly defined points since the lifetime of the intermediate ions can vary considerably, depending on the reaction conditions. The mechanism is not simply defined by the ease of removal of hydrogen or halogen but by the strength of the anion and the temperature. Under environmental conditions the transition state may be less clearly defined than the intermediates of the ElcB mechanism.

This proposed mechanism is supported by deuterium exchange studies for TCE reacting with deuterium oxide and sodium deuteroxide (Reference 18) or calcium deuteroxide (Reference 19).

In the study of deuterium exchange by Houser, et.al. (Reference 18) TCE was refluxed with approximately 6N sodium deuteroxide in deuterium oxide at 81-84 C. The half life for the exchange was 50 hours. During refluxing mild explosions (characteristic of the reaction of DCA with oxygen) occured with increasing frequency. The rate of decomposition to DCA was estimated at 0.12 percent per hour.

The reaction of TCE with base is spontaneous at room temperature. Possible bases include potassium, calcium or sodium hydroxide; sodium amide, or ethanolic alkali (Reference 20). These reactions can result in explosions due to the spontaneous autoxidation of the dichloroacetylene. Passage of TCE vapors over solid granulated potassium hydroxide at 130°C yields dichloroacetylene in 65 percent yield. When pure potassium hydroxide is used, the reaction is accompanied by evolution of flame and finally violent explosion (Reference 21). This reaction has been responsible for dichloroacetylene intoxication observed in patients inhaling TCE-containing air in closed recirculating systems equipped with alkali absorbers (Reference 22).

Daloze et.al. (Reference 23) examined the kinetic acidity of di- and trisubstituted halothenes. Measurements of hydrogen-deuterium exchange rates were determined in a sodium methoxide-methanol-O-d solution and selected results are summarized in Table 4. Olefins undergo base-catalyzed hydrogen-deuterium exchange faster than they undergo HX elimination or nucleophilic halogen substitution. The second-order rate constant for the exchange (acidity) of TCE is 150 times greater than for cis-1,2-dichloroethene and 200 times greater than for the trans isomer.

DCA has been formed in the gas phase above aqueous alkaline solutions with pH 11 to 13 and upon incubation with moderately alkaline material such as concrete (Reference 24). This indicates dehydrohalogenation can occur under relatively mild conditions. The goal of this study was to examine DCA as a possible intoxicant for person using TCE in the presence of mildly alkaline materials.

TABLE 4. RATES OF HYDROGEN-DEUTERIUM EXCHANGE ON SUBSTITUTED ETHENES IN CH_3OD/CH_3O^-

	$K \times 10^3$ $l \times MOLE^{-1} \times SEC^{-1}$
TCE	24.15
cis-DCE	0.16
trans-DCE	0.114

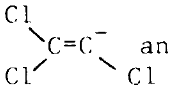
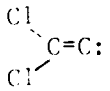
Samples were incubated at 40^{o}C for up to 72 hours and the ratio of DCA/TCE in the gas phase above the sample was determined. The method did not evaluate quantitative amounts of TCE which may have been transformed during the incubation. Since DCA is susceptible to further attack, and the loss of DCA may be faster than transformation of TCE, a steady state may be reached in the gas phase using this method. At pH 13 the ration DCA/TCE was 0.9 percent after 16 hours and 1.0 percent after 72 hours.

Noller and Klading (Reference 25) reviewed mechanisms for elimination reactions over polar catalysts. Although elimination reactions are known to proceed in the gas phase, the liquid phase and over solid catalysts, reactions in the liquid phase typically occurs at lower temperatures, in base, with an ionizing solvent. Liquid phase reactions are always accompanied by substitution, while gas phase reactions have a greater selectivity for elimination.

Another method for inducing a non-free-radical elimination reaction using an infrared laser, was described by Reiser, et al. (Reference 15). Free rotation around the double bond preceded elimination, and the dominant reaction of trans-DCE was observable isomerization to the cis-DCE which is thermodynamically more stable and less reactive under these conditions. Although the elimination reaction of TCE produced DCA, a different mechanism is suggested. The preferred mode was alpha to the chlorine atom. The preference for this type of elimination suggested that the reaction may proceed by formation of vinylidenecarbene ($Cl_2C{=}C:$), *followed by rearrangement* to form acetylene.

The formation of the carbanion or elimination product may be the limiting step for a number of potential rections of TCE including hydrolysis and various substitution reactions. The information for the kinetics of this reaction is inadequate to extrapolate to rates in dilute aqueous solutions typical in the environment. Water, as a more polar solvent, would tend to facilitate the information of the carbanion. The reaction is apparently second order, first order with respect to base. Polar catalysts can assist in the elimination reaction.

B. BASE CATALYZED ADDITION AND SUBSTITUTION REACTIONS

In the reaction of TCE with base two species with increased reactivity are possible: a carbanion:  $Cl_2C=C^{-}Cl$ and DCA: ClC=CCl. Vinylidene carbene:  $Cl_2C=C:$ is a reactive species noted only under laser studies. Many substitution and addition reactions of TCE are carried out in the presence of base and what initially may appear to be a direct substitution may in fact be a multistep process,using these intermediates. The first step would be the elimination producing dichloroacetylene; the second step then is a nucleophilic attack on the acetylene (Reference 26).

Rappaport (Reference 27) reviewed the mechanisms for nucleophilic vinylic substitution, including TCE and isomers of dichloroethene, providing comparisons of the behavior of these compounds. Figure 2 illustrates the two mechanisms, elimination-addition and addition-elimination. Rappaport reports:

1. Chlorine is displaced by a variety of nucleophiles which are more nucleophilic than the chloride. (Table 5)
2. The elimination occurs when chlorine is trans to the hydrogen. Cis-dichloroethene and TCE react by elimination in the first step.

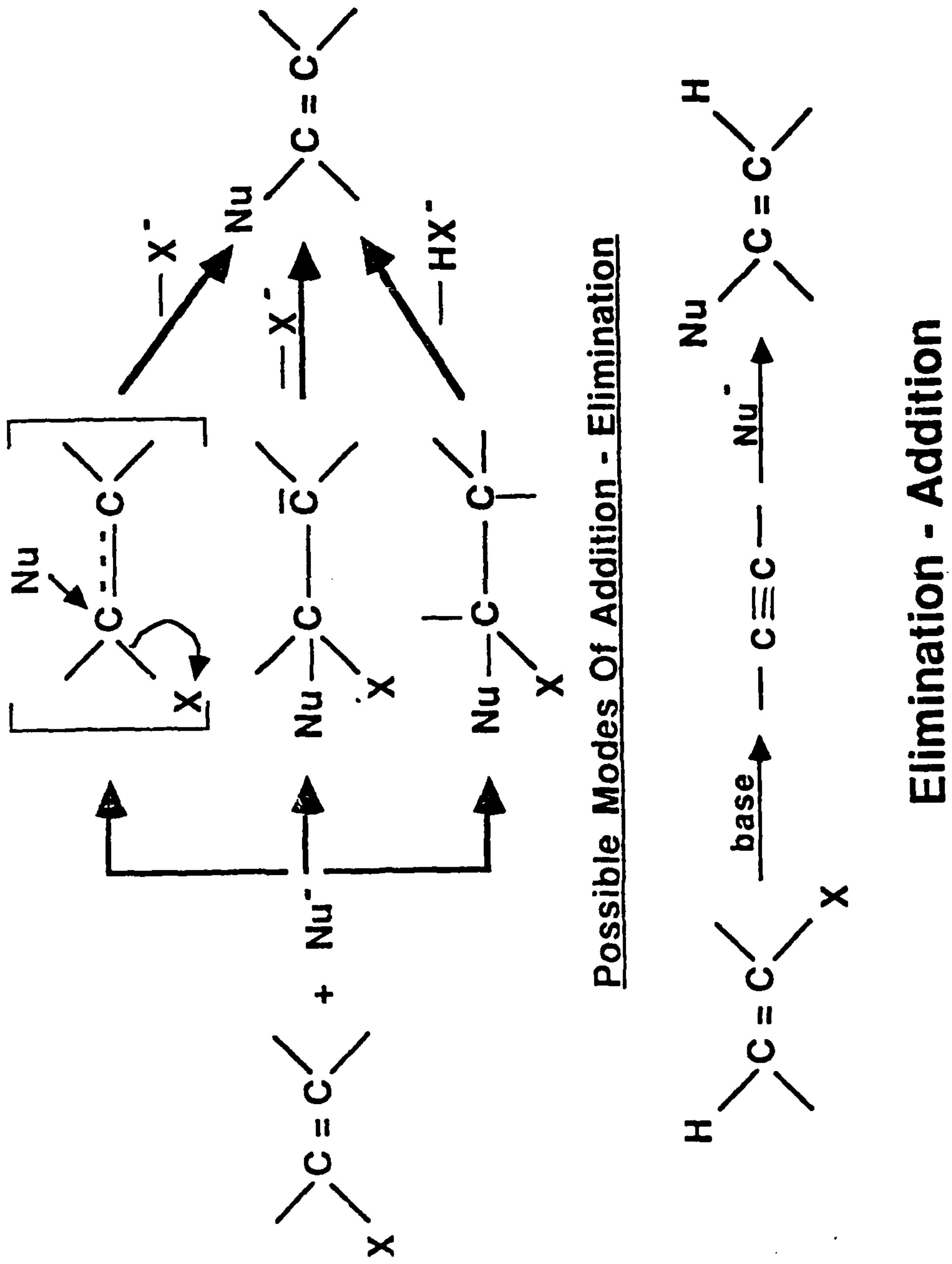


Figure 2. Nucleophilic Vinylic Substitution (Reference 27)

TABLE 5. RELATIVE NUCLEOPHILICITIES TOWARD B-CHLORO - - P - TOLUENESULPHONYLETHYLENE (REFERENCE 27)

Nucleophile	Relative Nucleophilicity
Cl^-, Br^-, I^-	ca. 10^{-7}
N_3^-	0.63
cyclohexylamine	1.0
MeO^-	28
PhS^-	174
$PhCH_2S^-$	4530

3. 1,1- and trans-1,2-dichloroethene react via addition-elimination. Trans elimination is possible for the 1,1-dichloroethene molecule. However, due to the reduced acidity of the hydrogen and electrophilicity of the Beta-carbon, this isomer reacts by addition-elimination.

4. Tetrachloroethene is active due to the four chlorine atoms. Since it has no hydrogen, it reacts by addition-elimination route.

5. Addition of the nucleophile produces a saturated carbanion intermediate. Various mechanistic routes are available for the carbanions formed by addition of nucleophiles to activated olefins. The retention of configuration for cis and trans isomers of olefins with an alpha-hydrogen suggests that the expulsion of the leaving group is faster than the addition of a proton to the carbanion.

6. For the addition-elimination route the rate determining step is the bond-making to the nucleophile, not rupture of the bond to the leaving group.

7. Elimination-addition requires a strong base to abstract the proton. This may compete for attack at the carbon. The base and the nucleophile used in many of the reactions are not the same. A strong base may be responsible for the elimination, while a weaker base but better nucleophile may add preferentially to the acetylene.

The formation of trisubstituted products consists of alternating elimination-addition with addition-elimination. (Example: Figure 3).

The organic synthesis reactions using this mechanism attempt to produce high yields of product. High concentrations of strong base are used, frequently using heat. Products for selected reactions are summarized in Table 6.

Pielichowski and Popielarz (Reference 28) found in the absence of the aliphatic amines, explosive mixtures of DCA and air are formed. This also occurs with less reactive aromatic amines under the phase-transfer catalytic conditions of the reaction. Dichloroacetylene concentrations do not build up when a reactive nucleophile is present.

Due to strong reaction conditions, many of the reported reactions go through the formation of DCA. Jonczyk et.al. (Reference 29) reported the reaction of the carbanion with carbon tetrachloride in a catalytic two-phase system, which produced an 80 percent yield of tetrachloroethene, according to the reaction sequence shown in Figure 4.

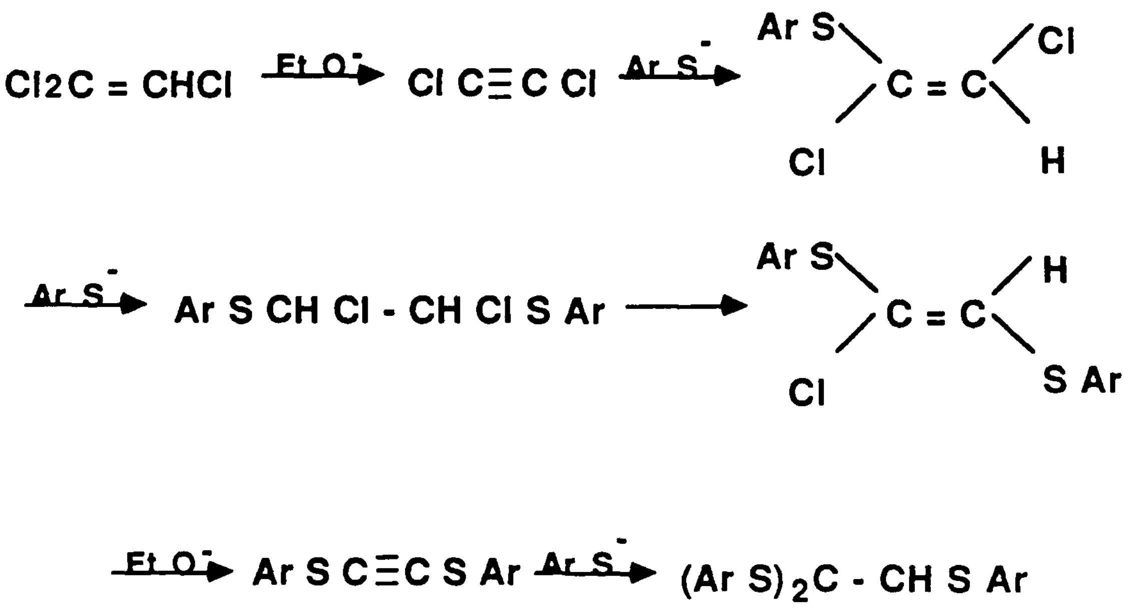
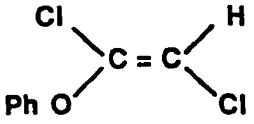
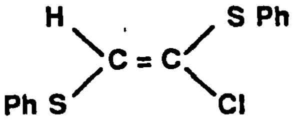
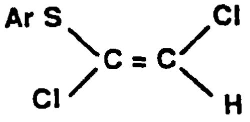
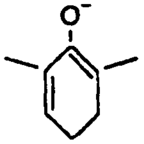
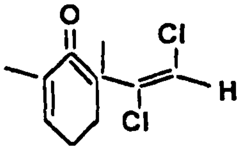
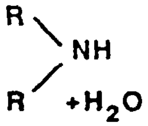
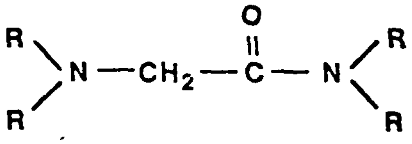


Figure 3. Formation of Trisubstituted Products of TCE with p-Toluene Thiolate Ion (Reference 27)

TABLE 6. NUCLEOPHILIC SUBSTITUTION REACTIONS OF TRICHLOROETHENE

Nucleophile	**Main Product**	REFERENCE
Ph O$^-$		30
Ph S$^-$		30
Ar S$^-$		26
		31
		28

Ph = Phenyl
Ar = Aryl

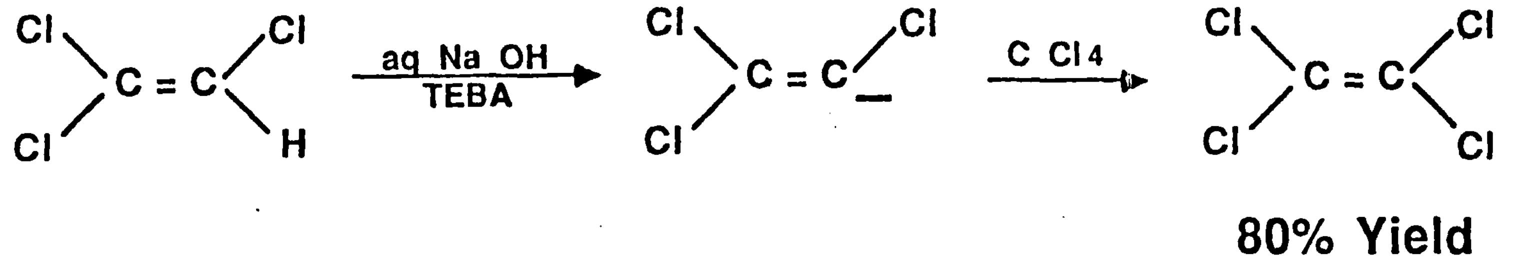
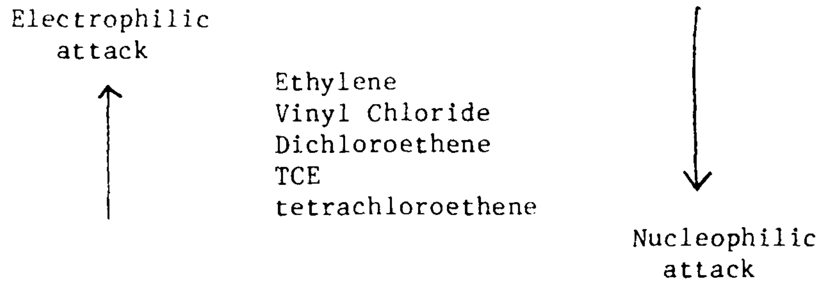


Figure 4. Catalytic two Phase Reaction of Trichloroethene and Carbon Tetrachloride (Reference 29)

In this reaction scheme, the proposed reactive intermediate is the carbanion. This suggests that, under certain conditions, enhanced reactivity may result without formation of the elimination product.

Comparisions of the susceptibility of simple olefins to attack is illustrated:



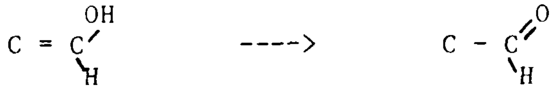
Vinyl chloride is more susceptible to attack by electrophilic reagents and is resistant to attack by nucleophiles. Polyhalogenated olefins show greater susceptibility to attack by nucleophiles.

The specific case of substitution of hydrogen for chlorine, or addition of hydrogen to the double bond are considered reduction reactions. These will be discussed in Section V.

The reaction of polychlorinated biphenyls (PCBs) in transformer oil with poly(ethylene glycols) and potassium hydroxide under phase transfer catalyzed conditions has been reported as a treatment method. Both the potential for attack as a nucleophile and the strongly basic conditions (both RO- and OH-) would promote formation of the carbanion, elimination product, and addition reactions in reactions with TCE in a fashion similar to its behavior with PCBs (Reference 32).

C. HYDROLYSIS

Hydrolysis is the chemical transformation occuring when a compound reacts with a solvent, typically water, which is in large excess. The overall reaction for most organic halides involves replacing a chlorine atom with a hydroxy (OH) group. In the case of alkenes this would be followed by rearrangement to an aldehyde as illustrated:



$$\mathrm{C = C}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\ }} \; \text{---->} \; \mathrm{C - C}\overset{\mathrm{O}}{\underset{\mathrm{H}}{\ }}$$

In general, alkenes are considered to be resistant to nucleophilic attack and hydrolysis, based on the following:

1. "Several classes of hydrolyzable compounds have not been included in this review because some are hydrolytically inert under ordinary conditions and are best considered as refractory toward water (nitriles, vinyl, and aromatic chlorides are examples),..." (Reference 33).

2. According to the Environmental Protection Agency (1975b), trichloroethene is not hydrolyzed by water under normal conditions." (Reference 3).

3. "The outstanding chemical characteristic of vinyl halides is their general inertness in S_N1 and S_N2 reactions."(Reference 12).

The most frequently referenced study for the rate of hydrolysis of TCE was by Dilling et al.(Reference 34). The rate constant was determined to be 0.065 + 0.001 mo^{-1}, with a half life of 10.7 months at 25° C and pH 7. Molecular oxygen was present and the degradation rate was suggested to be a result of oxidation as well as hydrolysis according to the authors.

In a study of hydrolytic decomposition by Pearson and McConnell volatilization was extrapolated to zero and they estimated a half-life for TCE of 30 months (Reference 35).

It is important to evaluate a contaminant's behavior with respect to water and oxygen to determine its environmental fate. Currently available information on the hydrolysis of TCE under environmental conditions does not clearly differentiate between the reaction with water and oxygen, nor does it specify a mechanism for the loss of TCE. Hydrolysis products were not identified. The rate of 0.065 mo^{-1} determined by Dilling, et al. (Reference 34) is used in modeling studies, however, the rate is considered a maximum and EPA suggests it does not truly represent hydrolysis.

Based on evaluation of the behavior of TCE, the formation of products may occur via a carbanion intermediate. Water as a polar solvent would support formation of a carbanion. Greim et al. (Reference 24) detected DCA upon incubation of TCE above an aqueous solution of pH 11. In the case of a dilute aqueous solution at pH 7, we cannot exclude the possibility that the substitution of hydroxide (OH) ion for chloride could occur with the carbanion, since the carbon-chloride bond is weakened under those conditions.

It may also be possible for the nucleophilic hydroxide (OH) ion to add to the double bond of TCE, followed by elimination of chloride. Under strongly basic conditions used in studies of nucleophilic substitution, TCE reacts by the elimination-addition mode. However, TCE should be more susceptible to nucleophilic attack than dichloroethene isomers which react by addition-elimination; and, under environmental conditions, this may be a preferred reaction pathway. Data on the rate of hydrolysis of DCE isomers was not available, however. Dilling et al. (Reference 34) obtained a rate for hydrolysis of tetrachloroethene of 0.079 mo^{-1} (half-life of 8.8 months). Tetrachloroethene is more susceptible to nucleophilic attack than TCE which is consistent with the higher rate. It has no acidic hydrogen, therefore, a carbanion or an elimination product would not be a predicted intermediates.

The overall rate of hydrolysis is the sum of the contribution by the acid and base catalysis rates and the rate in neutral water according to the following equation:

$$k_t = k_a[H+] + k_n + k_b[OH^-]$$

If the reactivity of TCE is enhanced by base, as suggested in the literature, the half-life may be decreased in aquifers with elevated pH.

In subsurface environments, volatilization is limited by rates of diffusion, and biodegradation is typically slowed by small populations of microorganisms. A half-life of 10.7 months for "hydrolysis" is a competing mode of attenuation under these circumstances.

SECTION IV

FREE RADICAL REACTIONS

A. BACKGROUND

Several reactions of TCE occur via a free radical mechanism. To clarify the behavior of TCE with respect to free radicals, degradation is examined under conditions of minimal amount of energy to initiate a reaction. Under conditions of higher energy inputs (eg., high temperatures or high energy radiation), a variety of free radicals will form and react, forming a greater number of products. Under these conditions it is more difficult to evaluate specific reaction mechanisms which may be characteristic of behavior in subsurface environments. During incineration or degradation in the troposphere, the high energy levels break many bonds of TCE including the carbon-carbon double bond. These reactions are briefly discussed.

Several texts provide extensive information on free radical reactions (References 36-39). The following information from these references will assist in clarifying research on specific free radical reactions involving TCE:

1. Formation of Free Radicals

Free radicals are molecules that contain one or more unpaired electrons and are formed by dissociation of a nonradical. The energy required to break bonds to form reactive free radicals is related to the bond energies in the molecules.

At temperatures below 100°C, thermal motion alone rarely can supply sufficient energy to break any significant number of bonds whose strength exceeds 30-35 kcal/mole to form reactive free radicals.

Methods used to generate free radicals include use of heat, light, high energy radiation, and/or peroxides.

2. Chain Reactions

When the energetics are favorable, free radicals induce a chain reaction in which each reaction results in the formation of another radical. Chain reactions are limited by termination processes which consume radicals. Propagation is favored over termination when the concentration of radicals is low enough so that the radicals are less likely to meet and terminate the chain reaction. The reactions are sustained by elevated concentrations of the participating molecules.

The overall rates of chain reactions are slowed by substances which can combine with radicals and convert them into products which do not participate in the chain-propagation steps. These are radical traps or inhibitors.

Molecular oxygen is a diradical which participates in many free radical processes but can also interfere with propagation steps. A small amount may initiate a reaction while a large quantity may retard or completely inhibit reactions and thus induce oxidative processes. Organic peroxide radicals which may form from free radical interactions with oxygen are comparatively less reactive and can usually terminate the chain.

Most studies of free radical reactions of TCE which will be discussed were performed in gaseous or liquid solvent phases. Some of the gas-phase studies are intended to mimic photodegradation, however, studies are not conducted under conditions which mimic the subsurface environment. Free radical conditions in the vadose zone and groundwater are not characterized.

Our approach to this problem is to examine patterns of behavior of TCE in response to attack by free radicals. Establishing trends in the mode of attack and relative reactivities of free radicals which have been studied, will allow predictions of the behavior of TCE in response to attack by radicals which may be present in the subsurface.

B. MECHANISM AND RELATIVE REACTIVITY

Trichloroethene reacts with a number of free radicals including: Cl, OH, CH_3, CCl_3, and cyclohexyl. These free radicals add to the double bond more easily than abstracting a hydrogen. The attack is

Anti-Markovnikov, that is the addition occurs on the carbon containing the hydrogen (Reference 40). The generalized reaction sequence is outlined in Figure 5.

As illustrated, the radical formed by addition to TCE may further react by hydrogen abstraction or unimolecular decomposition,yielding a chlorine atom and an olefin. The predominant pathway is determined by the reaction conditions (primarily temperature) and the specific radicals. A summary of primary products formed from free radical reactions with TCE is found in Table 7.

Kinetic data and reactivity of radical species are summarized in Tables 8 and 9. The radicals may be electrophilic ($Cl^{\bullet}$) or nucleophilic ($CCl_3^{\bullet}$). Addition of radicals to TCE is affected by both steric and polar effects.

Since the carbon-carbon double bond is characteristically susceptible to attack by electrophilic agents and the chlorines lower the electron density of the double bond, the reverse order of activity for attack on chlorinated ethene molecules would be expected from electrophilic radicals than from nucelophilic radicals. For the electrophilic chlorine (Cl) radical the relative reactivity for addition to chlorinated olefins is: cis-DCE > trans-DCE > TCE > tetrachloroethene. The documented order of reactivity for hydroxy (OH) radicals is : ethylene > vinyl chloride > TCE > tetrachloroethene.

The methyl radical is nucleophilic and attack would be easier on the olefins containing the greater number of chlorine atoms which withdraw electrons and make the double bond more susceptible to nucleophilic attack. However, tetrachloroethene is hindered and this

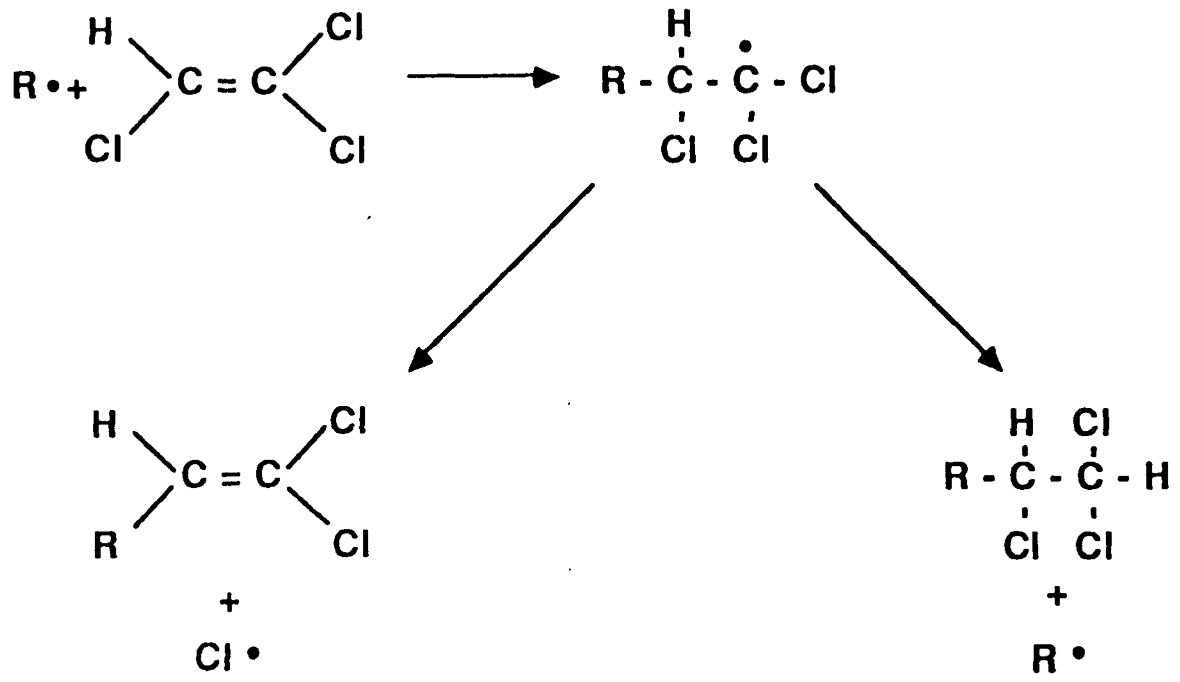


Figure 5. Free Radical Attack on Trichloroethene

TABLE 7. REACTION OF TCE WITH ALKYL RADICALS

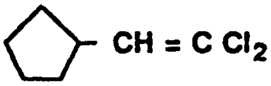
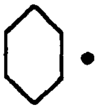
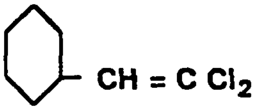
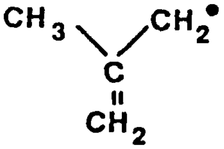
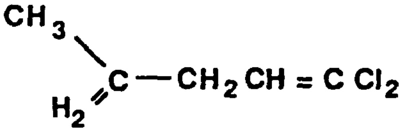
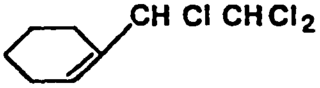
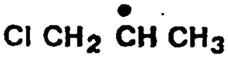
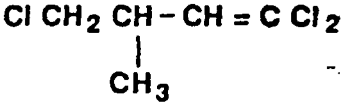
Alkyl Radical	Major Product	REFERENCE
		41
		42,43
$CCl_3\bullet$	$CCl_3CH=CCl_2$	44,45,46
		47
		48
$C_6H_5\bullet$	$C_6H_5-CHClCHCl_2$	48
$ClCH_2\overset{\bullet}{C}HCH_3$	$ClCH_2\underset{CH_3}{CH}-CH=CCl_2$	48

TABLE 8. KINETIC DATA FOR FREE RADICAL ADDITIONS (Reference 10)

Reaction	Log A 1 mole^{-1}S^{-1}	E Kcal mol^{-1}	Log k 1mol^{-1}S^{-1}
Chlorine Radical +			
Vinyl Chloride	9.5 - 10.3	0 - 1.5	8.8 - 10.2
cis-DCE	9.4 - 10.9	8.7 - 10.78	8.7 - 10.78
trans-DCE	10.48	-0.17	10.60
TCE	9.6 - 10.54	0 - 1.5	9.1 - 10.54
Tetrachloroethene	8.4 - 9.41	-0.5 - 0	8.7 - 10.1
Chloromethylidyne Radical (CCl) +			
TCE	-	-	^{2}9.60
Tetrachloroethene	-	-	^{2}10.0
Trichloromethyl Radical +			
Vinyl Chloride	6.4 - 8.7	3.4 - 7.6	4.65 - 7.6
trans-DCE	-	-	3.46
TCE	-	-	3.96
Tetrachloroethene	-	-	<2.24

TABLE 9. COMMON FREE RADICALS IN DECREASING ORDER OF ACTIVITY (REFERENCE 9)

Radical	E (kcal/mole) [a]
$F^{\cdot}$	0.2
$Cl^{\cdot}$	1.0
$H^{\cdot}$	8.7
$CH_3^{\cdot}$	11.2
$Br^{\cdot}$	13.3

[a] Activation energy for $X^{\cdot} + C_2H_6 \dashrightarrow XH + C_2H_5^{\cdot}$

reduces its susceptibility to attack. The overall order of reactivity for attack by methyl radicals on chlorinated olefins is: TCE > DCE > vinyl chloride > tetrachloroethene. The reduced reactivity of tetrachloroethene from predictions based on polar effects is attributed to steric hindrance.

In early copolymerization studies the relative rates of addition of acrylonitrile, vinylacetate and styrene radical were determined. The order of reactivity established was: vinylidene chloride > vinyl chloride > TCE > trans-DCE >cis-DCE >tetrachloroethene.

Anomalies, therefore, exist and make it difficult to predict reactivity order. For example, vinyl chloride is more reactive than ethylene in its reactions with electrophilic radicals such as trichloromethyl. Even though radicals may be electro- or nucleophilic, these tendencies are slight compared to electrophilicity of a positive ion or nucleophilicity of a negative ion. The predominant character of a free radical is neutral, whether it has slight electrophilic or nucleophilic tendencies (References 9 and 43).

C. REACTION CONDITIONS

Free radicals contain one or more unpaired electrons, and these are formed by dissociation of a nonradical. The energy required to initiate or sustain a free radical reaction is related to the bond energies in the molecules. Methods of generating free radical include addition of heat, photodissociation, addition of high energy radiation, and/or addition of peroxides.

Many documented reactions are performed under atypical environmental conditions, with the exception of studies producing data on potential rate of photodegradation in the troposphere. The conditions generally produce condensation products as described in the previous section. Appendix A summarizes the primary products and reaction conditions for a number of free radical reactions.

The potential for free radical addition reactions to occur in the environment depends on the specific conditions and presence of required reactants. Many of the reactants studied (isobutene, cyclohexane, triethyl silane, etc.) are unlikely to be present in sufficient concentrations to react with TCE. These reactions demonstrate types of products which may result under free radical conditions.

The following sections provide a more detailed analysis of specific free radical reactions which have environmental significance.

1. Photolysis/Atmospheric Degradation

Considerable research has been done on the photodegradation of contaminants, including TCE. Standard protocols for estimating the length of time a pollutant would remain in the troposphere require investigating the extent to which TCE reacts with hydroxy free radicals. The hydroxy free radical is considered the principal scavenging mechanism for TCE and many other halogenated compounds in the atmosphere. EPA (Reference 51) summarized a number of studies which estimated the atmospheric lifetime for TCE. The estimates ranged from 54 hours to approximately 15 days.

Sanhueza et al. (Reference 52) reviewed oxidation of haloethenes, including Cl-atom-initiated oxidation, mercury sensitization, and reactions with atomic oxygen and ozone. Many of these reactions involve excess energy, sufficient to break the carbon-carbon bond and form a variety of oxidation products. Products from atmospheric oxidation of TCE include dichloroacetyl chloride, carbon monoxide and phosgene (Reference 53).

The rate constants for the reaction of hydroxy radicals with TCE is approximately 14 times faster than reaction with tetrachloroethene (Reference 54).

The mechanism for the hydroxy-olefin reactions involves an initial attack on the carbon-carbon double bond, giving an excited ethyl radical complex. When the ethylene contains a chlorine atom on the carbon to which the OH is bonded, the chlorine may be ejected. The carbon-chlorine bond is generally about 10 kcal/mole weaker than the carbon-hydroxy bonds and the complex is sufficiently activated to release a chlorine radical (Reference 55).

2. Pyrolysis

Trichloroethene reacts much more slowly than the saturated compounds such as tetrachloroethanes, from which it may be derived pyrolytically. Goodall and Howlett (Reference 17) reported the initial rection was the dehydrochlorination of TCE at temperatures between 385°C and 445°C. The initial dichloroacetylene rapidly and completely polymerises to hexachlorobenzene.

When heated to 700° C, TCE decomposes to form products such as methylene chloride, dichloroethene, chloroform, carbon tetrachloride, perchloroethene, 1,1,1,2-tetrachloroethane, pentachloroethane, hexachlorobenzene, and 2,3,5,6,-tetrachlorobenzotrichloride. Pyrolysis of TCE in air yields carbon dioxide and hydrochloric acid only as long as not more than 12 mg. TCE per liter of air is present. At higher concentrations, up to 20 percent of the total carbon and chlorine present is converted to carbon monoxide and chlorine, but phosgene is not formed at concentrations up to 100 mg. per liter of air (Reference 21). Reactions at elevated temperatures consist of radical and unimolecular elimination mechanisms (Reference 56).

3. Polymerization

Although TCE can copolymerize with vinyl compounds, it does not readily polymerize by itself. This has been interpreted as an indication that the specific rate constant for the self-propagation step is unusually low, rather than as evidence for a low rate of chain initiation or for an unusually high rate of chain termination (Reference 57). Copolymerization studies have been conducted (Reference 58) and patents have been issued, although none have significant commercial significance.

SECTION V

REDUCTION

Two types of reduction of TCE are possible: (1) replacement of chlorine by hydrogen (2) addition of hydrogen to the double bond. Mechanisms for the reduction of organic compounds are poorly defined, and, in some circumstances, free radical mechanisms are implicated. In the context of potential environmental reactions we are concerned with homogeneous or heterogeneous catalyzed reactions, particularly using molecules other than molecular hydrogen as the source of hydrogen.

A number of mechanisms have been postulated including transfer of a hydride ion or a two-step electron transfer process. These transfers can occur with interaction between TCE and organic molecules which are more reduced than the TCE molecule. Organic compounds which have been used as hydrogen donors in studies of homogeneous and heterogeneous catalytic transfer hydrogenation are included in Table 10. In principle, the donor can be any organic compound whose oxidation potential is sufficiently low enough for the hydrogen transfer to occur under mild conditions (Reference 59). Many of these compounds are likely to be present in areas where anaerobic biodegradation is occuring.

The role of the catalysts in these reduction reactions is unclear. They may form intermediate bonds during the transfer process. Metals may have salts suitable for donation of electrons. Typical catalysts used for reduction of organics in synthesis

TABLE 10. EXAMPLE OF HYDROGEN DONORS FOR CATALYTIC TRANSFER HYDROGENATION (REFERENCE 64)

cyclohexene
limonene
dihydrofuran
ethanol
propan - 2 - 01
benzyl alcohol
hydroquinone
tetrahydrofurfurol
steroids
sugars

1,2 - ethanediol
ascorbic acid
phenols
formic acid
formates
phosphinic acid
hydrazine
phosphorous acid
metal hydrides

TABLE 11. ELEMENTS USED IN CATALYTIC REDUCTIONS (REFERENCE 64)

Palladium	(Pd)
Platinum	(Pt)
Ruthenium	(Ru)
Francium	(Fr)
Rhodium	(Rh)
Iron	(Fe)
Nickel	(Ni)
Cobalt	(Co)
Molybdenum	(Mo)
Osmium	(Os)
Magnesium	(Mg)
Aluminum	(Al)

reactions are summarized in Table 11. Enzymes would be specialized organic catalysts and there have been attempts to mimic enzymes with simple model compounds with a NADH-like reaction. Yasui et al. (Reference 60) reported on the use of such a model for the free radical reductive debromination of vic-dibromides to alkenes.

Heterogeneous dehalogenations may occur with zinc in protic solvents or magnesium, lithium or sodium in ethereal solution. In general, the elimination occurs at the surface of the metal. It is likely that the metal donates electrons and that carbanions, rather than radical processes, are favoured (Reference 61).

A. CARBON-HALOGEN BOND

Reduction products such as dichloroethene isomers or vinyl chloride have been found as TCE degradation products at solvent-contaminated sites. The degradation is accelerated in biologically active samples. However reduction products were detected in sterile controls which implies possible abiotic mechanisms. Abiotic degradation in anaerobic soils and sediment-water systems has been observed for other chlorinated contaminants (Reference 62). There is a question whether the dechlorination process may be related to the lower oxidation-reduction (redox) potential of active systems, the organisms likely playing an indirect role by producing a stronger reducing environment.

Chemical reduction of chlorinated hydrocarbons is supported by observations of comparable transformation in electrochemical systems, although it is not possible to treat these systems like inorganic compounds. The experimental voltages could be used to give a relative index of the tendency to breakdown by a reductive mechanism. Stickney et al. (Reference 63) surveyed a number of compounds to determine their stability with reference to platinum electrodes. Adsorbed carbon-carbon double bond compounds including TCE were susceptible to both hydrogenation and to oxidation, although the peak potentials for the reduction reactions were indistinct.

In a recent review of heterogeneous catalytic transfer hydrogenation , Johnstone et al. (Reference 64) stated that catalytic cleavage of carbon-halogen bonds is usually a reaction to be avoided rather than encouraged for industrial application or organic synthesis. It appears that numerous reducing agents and catalysts can be used to reduce the carbon-halogen bond, but specific reaction of these with TCE was not specified.

Nakamura (Reference 65) found alkenyl halides were less reactive than alkyl halides toward MoH_2 $(n-C_2H_5)_2$, and lists TCE as having no or slight reaction after one day at room temperature. A free radical mechanism was implicated for reactions occurring with that reducing agent.

Green and Knowles (Reference 66) showed that TCE is reduced by Bis-(n-cyclopentadienyl) dihydridotungsten $(n-C_5H_5)_2$ WH_2. The reaction products were 91 percent cis-1,2-dichloroethene, 9 percent trans isomer and 3 percent 1,1-dichloroethene. The reaction was carried out at 100^{o} C for 2 days. This is of particular interest because the dominant isomer identified by Parsons et al. (Reference 5) in studies of anaerobic degradation of TCE was also the cis isomer.

The kinetics for the chemical reduction were not specified. Table 12 summarizes the reaction temperature, apparent reaction completion time, and products for tetrachloroethene, TCE,

TABLE 12. REDUCTION OF HALOGENATED ALKANES AND ALKENES BY BIS (N-CYCLOPENTADIENYL) DIHYDRIDOTUNGSTEN (REFERENCE 66)

HALOGENOCARBON	REACTION TEMP (C)	TIME	PRODUCTS
Carbon tetrachloride	20	1min	Chloroform
Chloroform	20	18hrs	Dichloromethane
Dichloromethane	70	8day	Chloromethane
Hexachloroethane	20	15min	Pentachloroethane
Pentachloroethane	20	20min	1,1,2,2-Tetrahloroethane
1,1,2-Trichloroethane	102	18hrs	1,2,-dichloroethane
Tetrachloroethene	100	12hrs	Trichloroethene
Trichloroethene	100	2day	cis-1,2-dichloroethene (91%)
Dichloroethenes	120	2day	Ethylene
Vinyl chloride	120	3day(a)	Ethylene

(a) reaction incomplete

dichloroethenes, and vinyl chloride. The hydrogenolysis reaction becomes increasingly difficult with each subsequent removal of chlorine from the molecule. The reaction of vinyl chloride was incomplete after 3 days at 120°C.

This increasing resistance to futher reduction of TCE degradation products is consistant with behavior observed in biodegradation studies (Reference 62). This trend was also observed with other chlorinated hydrocarbons where compounds in a homologous series, showed the hydrogenolysis proceeds under the highest redox potentials for the most highly chlorinated compound (e.g. hexachlorobenzene: -1.322 V.; pentachlorobenzene: -1.573 V) (Reference 1). The most highly oxidized (chlorinated) species are the most easily reduced.

Trialkyl- or arylsilanes and stannanes have been used for the reductive hydrogenolysis of carbon-halogen bonds (Reference 64). Aloni et al. (Reference 67) reported on the free radical reaction of TCE with triethylsilane. The main products of the gamma-radiation induced reactions were: cis- and trans- dichloroethene, triethylchlorosilane, dichlorovinyltriethylsilane, and hydrogen chloride. The last three of these products are formed by the two-step process· addition of the Et3Si· radical, followed by unimolecular chlorine elimination. This is consistent with other proposed free radical interactions of TCE.

The formation of dichloroethenes is proposed to occur by the sequence outlined in Figure 6. The first reaction is a bimolecular chlorine transfer which produces a vinyl radical. This is not the typical mode of action of TCE interactions with free radical, and vinyl radicals are more typically formed by addition to triple bonds.

$$\mathrm{Et_3\,Si\bullet + TCE \longrightarrow Et_3Si\,Cl + CH\,Cl = C\,Cl\bullet\,[1]}$$

$$\mathrm{or \bullet CH = C\,Cl_2\ \ [2]}$$

$$\mathrm{[1] + Et_3\,Si\,H \longrightarrow cis\ or\ trans - DCE + Et_3\,Si\bullet}$$

$$\mathrm{[2] + Et_3\,Si\,H \longrightarrow 1,1 - DCE + Et_3\,Si\bullet}$$

Figure 6. Formation of Dichloroethenes from Triethylsilane Radicals ($Et_3Si\bullet$) and TCE (Reference 67)

The authors also report that when both cis and trans isomeric products are formed in the liquid phase from vinyl radicals, the relative yields of the isomers are controlled by the stability of the products. The reported ratio of the cis to trans isomer is 3.48 ± 0.59, which is higher than the ratio of 2 determined from gas phase photochlorination studies. The cis isomer has, therefore, been demonstrated to be the most stable in both gas and liquid phase studies.

Pitzer and Hollenberg (Reference 68) investigated the thermodynamic properties of cis- and trans- dichloroethenes and found the cis isomer to be 445 ± 20 cal./mole lower in energy at 0° K. This is an exception in that trans isomers are more typically of lower energy. The dominance of the cis isomer as a reduction product would be expected, therefore, regardless of the specific mechanism of the reaction.

Reductive dechlorination of chlorinated methanes and ethanes by reduced iron (II) porphyrins was examined by Klecka and Gonsior (Reference 69). Reduced iron porphyrins have been shown to catalyze the dechlorination of a variety of organochlorine compounds, including DDT, mirex, toxaphene and hexachloroethane. For their system of an aqueous solution containing hematin and a reducing agent, the reaction of reduced iron porphyrin was limited to the aliphatic molecules with three or more chlorine substituents on the same carbon atom. Thus, TCE was found to be unreactive. Other unreactive compounds included methylene chloride, 1,1,2-trichloroethane and 1,1-dichloroethane. 1,1,2,2-tetrachloroethane formed TCE via a dehydrodehalogenation reaction (elimination), rather than forming 1,1,2-trichloroethane via reductive dehalogenation.

The iron (Fe^{2+}/Fe^{3+}) couple has been postulated as the dominant redox system in the environment. Ferrous iron has been previously shown to catalyze the degradation of DDT and toxaphene under anaerobic conditions. Cytochrome P-450 has been shown to catalyze reductive dehalogenation reactions and it is postulated that other catalysts may include cyctochromes, flavoprotens, hemoproteins, chlorophylls and iron-sulfur proteins. Reactivity of these with respect to TCE was not reported.

B. HYDROGENATION OF THE CARBON-CARBON BOND

Addition of hydrogen to TCE is a possible mode of reduction of the double bond but is of little industrial importance since TCE is manufactured by elimination from the saturated compounds. The reduction products formed via hydrogenation of TCE and related anaerobic degradation products are:

Reactant	Product
TCE	1,1,2-trichloroethane
1,2-dichloroethene	1,2-dichloroethane
1,1-dichloroethene	1,1-dichloroethane
vinyl chloride	chloroethane

Most carbon-carbon double bonds, whether substituted by electron-donating or electron-withdrawing substituents, can be catalytically hydrogenated, usually in quantitative or near-quantitative yields. Hydrogenations in most cases are carried out at room temperature and just above atmospheric pressure. Trisubstituted double bonds such as found in TCE may require higher pressures, presumably due to resistance caused by steric factors. Hydrogenation of dichloroethenes and vinyl chloride should therefore be easier, although no specific data comparing these rates were found. Most catalytic reductions of double bonds have been shown to be cis, with the hydrogens entering from the less hindered side of the molecule (Reference 9).

Reduction can also occur by heterogeneous catalytic transfer hydrogenation using molecules other than molecular hydrogen. This process has been reviewed by Johnstone et al. (Reference 64). However, specific reference to their effectiveness with halogenated olefins was not addressed. Many of these organic hydrogen donor compounds may be present in anaerobic microbiologically active environments such as found in municipal landfills.

In a recent study by Lage and Parsons (Reference 70) cis-1,2-dichloroethene was degraded under anaerobic conditions to both vinyl chloride and chloroethane, with chloroethane in higher quantities. Apparently, reduction of the double bond by addition of hydrogen becomes competitive with reduction of the carbon-halogen bond when fewer chlorine atoms are present on the molecule.

Chloroethene was not a measured degradation product from trans-1,2-dichloroethene or 1,1-dichloroethene. The greater ease of saturation of the cis isomer may be related to the tendency of the reduction to add cis from the less hindered side of the molecule. This observed biological degradation pathway is not inconsistent with the predicted chemical behavior of these halogenated olefins.

C. SUMMARY OF OVERALL REDUCTION PATHWAYS

The ease of reduction by hydrogenolysis of vinyl halides is: Tetrachloroethene > TCE > dichloroethenes > vinyl chloride while the ease of reduction via addition of hydrogen to the double bond is: vinyl chloride > dichloroethenes > TCE

If the addition occurs by cis addition, where both hydrogens add to the same side of the double bond, less steric hindrance would occur with cis-1,2-dichloroethene than with 1,1-dichloroethene or the trans isomer. This mechanism is proposed for a number of catalytic hydrogenation reactions and is consistent with observations in biologically mediated systems.

Products of the reductive dehalogenation of TCE have been observed in the field as well as in laboratory studies. The reduction is thought to be primarily biological; however, degradation patterns are consistent with anticipated chemical reduction. Mechanisms are not clearly established but at least some of the dehalogenation appears to be abiotic.

SECTION VI

OXIDATION

Under the appropriate conditions, TCE has been shown to biodegrade aerobically, producing CO_2 and HCl. This biological oxidation is thought to occur via the monoxygenase enzyme systems in methanotrophs and this is discussed in Section VII. Atmospheric oxidation reactions occur via free radical mechanisms and are discussed in Section IV.

This section will briefly outline oxidation reactions which are not specifically discussed in other sections and which primarily involve the addition of oxygen to the carbon-carbon double bond.

Base-catalyzed reactions of TCE with subsequent hydrolysis or oxidation of the DCA constitute one method for ultimate oxidation of TCE.

To predict behavior of organic compounds toward oxidants requires knowledge of the mechanism of the reaction as well as comparative strengths of the oxidizing agents. Specific data on the chemical reactivity of TCE in oxidizing environments were not available for many agents.

Stickney et al. (Reference 63) examined the stability of a variety of compounds to electrochemical oxidation. The peak potential for the oxidation for many of the compounds, including hexafluorobenzene and limonene, were similar. The data suggest a possible platinum electrode surface phenomena.

A. AUTOXIDATION

The reaction of molecular oxygen with organic compounds at normal temperatures and without flame or spark is termed autoxidation. The reaction is catalyzed by light. The hydroperoxides produced often react further, to alcohols, ketones, and more complicated products, so that the reaction is not often used for preparative purposes.

Oxygen itself (a diradical) is too unreactive to be the species which actually abstracts a hydrogen. But if a trace of free radical is produced by some initiating process, then it reacts with oxygen to give the organic peroxide (R-O-O'); and this radical does abstract hydrogen in a chain reaction (Reference 9).

In at least some cases in alkaline media, a radical may be produced by formation of a carbanion and its oxidation by O_2 to a radical: $R\text{-}H + \text{base} \dashrightarrow R^- + O_2 \dashrightarrow ROO^-$.

From the industrial point of view, the autoxidation is one of the more important reactions of TCE. Many patents have been issued for stabilizers to inhibit this reaction. The degradation is believed to proceed either by dimerization to form hexachlorobutene, or by addition of oxygen to form intermediates as shown on Figure 7. Autoxidation gradually transforms pure TCE to dichloroacetyl chloride, hydrochloric acid, carbon monoxide, and phosgene (Reference 16).

Liquid-phase autoxidation of trichloroethene was studied by Mayo and Honda (Reference 71). Reactions were performed at 50 C, mostly with oxygen at a total pressure of about 40 psig. About 8 percent of the TCE was converted to $COCl_2$, CO, and HCl, the remainder to roughly equal proportions of dichloroacetyl chloride ($Cl_2CHCOCl$) and trichloroethene oxide. The liquid-phase oxidation is distinguished by formation of trichloroethene oxide and by a thermal initiation as

Figure 7. Possible Intermediates in the Autoxidation of Trichloroethene (Reference 16)

compared to the chlorine-sensitized gas-phase autoxidation as described by Sanhueza et al (Reference 52). Conversion in the liquid phase autoxidation proceeded at a steady rate of about 2.5 percent per hour at 40 psig. of oxygen and 0.7 percent per hour at 10 psig.

There is evidence that autoxidation decomposition can proceed by both free radical and ionic mechanisms. The environment of an autoxidation is very important in promoting and directing the reaction (Reference 72).

B. OZONE

Rate constants for the reaction of TCE with ozone in the gas and liquid phases have been measured (References 73, 74, 75). The second-order rate constants (k) for the reactions of ozone with olefins in CCl_4 solutions are (Reference 73):

Olefin	k, l. $mole^{-1}$ sec^{-1}
Tetrachloroethene	1.0
TCE	3.6
1,1-DCE	22.1
cis-DCE	35.7
trans-DCE	591
Vinyl chloride	1,180
Ethylene	25,000

The half-life for the reaction of ozone (40 ppb) and TCE in simulated ambient tropospheric conditions was greater than 390 days. This can be compared to the reaction with hydroxy radicals discussed earlier which give a half life of approximately 6 days (Reference 74).

Williamson and Cvetanovic (Reference 75) measured the second-order rate constants for halogenated olefin compounds in a carbon tetrachloride solution at room temperature. Increasing the number of chlorine atoms on the molecule substantially reduces the reactivity of the molecule toward ozone.

Ozone is an electrophilic reagent and the presence of chlorine atoms on an alkene reduces the electron density of the double bond. In addition, steric hindrance is postulated to affect the reactivity.

The ozonation of alkenes is quite sensitive to electronic effects, with electron-deficient alkenes like TCE reacting orders of magnitude slower than electron-rich alkenes. The rate of reaction of trans-DCE is about 25 times that of cis-DCE or 1,1-DCE. A general trend toward less negative entropies of activation with lower E_a suggests the possibility of a change in mechanism for more electron-rich alkenes (Reference 76).

C. HETEROGENEOUS PHOTOCATALYSIS BY TITANIUM DIOXIDE

Recent studies (References 77-82) demonstrated rapid degradation of TCE and other chlorinated compounds in dilute aqueous solution by irradiating a titanium dioxide (TiO_2) catalyst. An aqueous solution of 50 ppm of TCE would be mineralized in 2 or 3 hours by this process.

TiO_2 is a semiconductor which contains acidic and basic sites. Photogenerated electrons create a highly reactive surface with sufficient excess energy to break a number of bonds and form free radicals.

Based on our review we postulate some reactivity is due to formation of a carbanion or elimination product intermediate. This is based on the following evidence:

1. Nature of the catalyst.

Titanium oxide (TiO_2) is a semiconductor which contains acidic and basic sites. Under near-UV illumination the concentration of Ti(III) is increased by Ti(IV) reduction by photogenerated electrons. The surface is polarized.

Elimination reactions are promoted by polar catalysts, and semiconductors were mentioned as promoters of reactions which occur by the ElcB mechanism (Reference 61).

2. Products of the reaction

An intermediate in the degradation of TCE is dichloroacetaldehyde. Degradation of 1,2-dibromoethane (EDB) produced vinyl bromide as an intermediate, while a trace of vinyl chloride formed from 1,2-dichloroethane. This indicates that elimination is a possible reaction process.

3. Inhibition of the reaction by acid

The dehalogenation reactions were noted to be inhibited by acid, particularly when the pH approached the pK_a of the TiO_2 surface at 3.5-4.5. This is consistent with the promotion of the reaction under base catalyzed conditions.

4. Relative rates of degradation

In examining the reactivity of a particular homologous series such as the chlorinated methanes differences in rates were measured. Since the surface is highly active all of the chlorinated methanes examined were mineralized to CO_2 and HCl during photocatalysis with $Ti)_2$. The relative rates were in the approximate ratio of 29 (trichloro-) : 9 (dichloro-) : 1 (tetrachloromethane).

For the chlorinated ethene series rates were measured for TCE and tetrachloroethene. The rate for TCE degradation was greater than for tetrachloroethene. Data were not available for other compounds in the series.

The relative reactivities may reflect both the ability to form a carbanion or carbene, as well as reactivity toward hydroxy radicals which are postulated to form under the conditions of the reaction.

In aqueous solution, the surface of the TiO_2 is covered by hydroxyl groups as well as molecular water. The formation of hydroxy radicals has been postulated for a number of reactions and has been verified in the case where oxygen was present in addition to the illuminated TiO_2. Complete mineralization of chlorinated methanes and ethanes required the presence of oxygen.

D. INTERMEDIATE COMPOUNDS

Metabolic intermediates formed during breakdown of TCE include epoxides and chloral as illustrated in the scheme outlined in Figure 8. Molecular rearrangements in which a chlorine migrates from one carbon to the other have been noted also in studies of oxidation by organic peroxides. The migration is thought to occur as a result of formation of an ion pair at the intermediate epoxide stage (Reference 83).

In studies of reactivity of TCE with superoxide (O_2^-), rates were determined to be not significant in dimethyl sulfoxide. However, cis-DCE, TCE and tetrachloroethene are rapidly oxygenated by superoxide in dimethylformamide (Reference 84). Superoxide acts as a strong base due to its nucleophilic character, and some of the reactivity appears

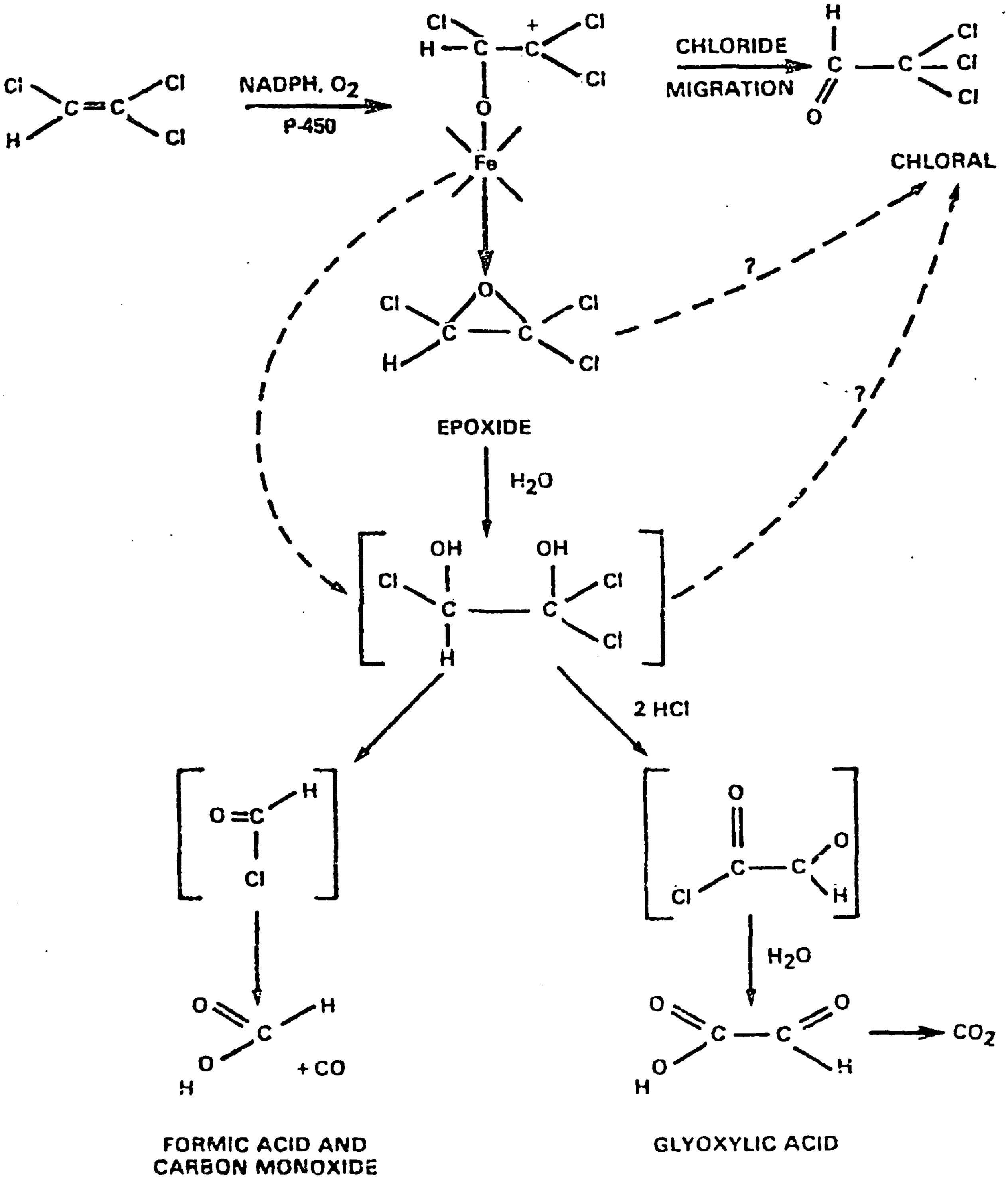


Figure 8. Postulated Scheme for the Metabolism of TC (Reference 85)

related to an intermediate elmination reaction with subsequent reaction of the ethyne with superoxide. The slower reaction rates in dimethyl sulfoxide are attributed to a leveling effect of both the nucleophilicity and basicity of superoxide in that solvent. Reaction intermediates were postulated to be vinyl peroxy radicals, chloroacyl radicals and phosgene. Only the final products of bicarbonate and chloride ions were identified.

SECTION VII

BIODEGRADATION

A. BIODEGRADATION OF TRICHLOROETHENE

The biodegradation of trichloroethene has been studied mostly in aquifer materials and somewhat less in soils and sewage treatment plants.

The biodegradability of 114 organic priority pollutants in wastewater treatment plants was investigated (Reference 86) using a static culture flask-screening procedure (Reference 87). Wastewater was amended with yeast extract and spiked with 5-10 mg/L of the test compounds. The flasks were incubated for 7 days at 25C in the dark. This was followed by three 7-day subcultures. TCE, at initial concentration of 5 mg/L was degraded up to 87 percent in 7 days. The volatilization loss was 22-29 percent at the incubation temperature used.

Two recent studies have dealt with TCE degradation in soils (Reference 88,89). A soil from Des Moines, Iowa, was spiked with 2000 ppm of labeled TCE and incubated under anaerobic conditions in vials sealed with teflon septa. Degradation was determined, taking into account losses via adsorption to soil and volatilization. It was observed that TCE degradation was of biological origin since dichloroethylene (DCE) was detected in all the unsterilized soil samples. Only 1,2-DCE was observed (Reference 88). The authors speculated that DCE could be further degraded to vinyl chloride in soils.

Wilson and Wilson (Reference 89) considered another approach in studying TCE degradation in soils. Sandy soil columns were leached with 150 ug/L TCE and further exposed to air containing 0.6 percent natural gas having the following composition: 77 percent methane, 10 percent ethane, 7 percent propane, 2.4 percent n-butane, 1 percent isobutane + other hydrocarbons. It was noted that TCE was degraded to CO_2 and that the biological transformation was an aerobic process. Biological activity was responsible for TCE removal by one order of magnitude following a 2-day residence time. It is speculated that methylotrophs (i.e., aerobic bacteria growing on one-carbon compounds), particularly methanotrophs (i.e., aerobic bacteria using methane as a source of carbon and energy), may be involved in the biological transformation of trichloroethene (References 90 and 91). Thus, the Wilson and Wilson's approach consisted in enriching the soil for methanotrophs which will subsequently oxidize trichloroethene. Following an electron microscopic study undertaken by Ghiorse and Blackwill (Reference 92) it was suggested that some of the bacteria observed in subsurface materials were methane - oxidizing bacteria. The application of this concept to aquifers will be discussed later.

In Palo Alto, California, Roberts and his collaborators (Reference 93) have studied the injection of reclaimed tertiary effluents into aquifers. Fifty days after cessation of injection, it was observed that the concentration of chloroform and other trihalomethanes have decreased significantly whereas a slow decrease was noted for trichloroethene and tetrachloroethene. Anaerobic conditions were presumed to prevail under field situation. TCE transformation under laboratory conditions was subsequently undertaken by various research teams to confirm the field data.

The biological transformation, particularly the dehalogenation, of chlorinated aliphatic hydrocarbons in groundwater was discussed in three recent reviews (References 94, 95, and 96). Three experimental approaches have been considered for the study of biodegradation of this class of chemicals: (1) TCE degradation in batch cultures in the presence of a chemically defined medium. (2) TCE transformation in the presence of glass beads, using continuous - flow fixed film systems. (3) TCE transformation in actual aquifer materials.

Bouwer et al. (Reference 97) investigated the degradation of 1- and 2-carbon compounds, including TCE, in batch cultures of sewage microorganisms under aerobic (initial D.O. = 8 - 9 mg/L) and anaerobic conditions. The anaerobic bottles were seeded with a mixed culture of methanogenic bacteria obtained from a digester whereas the aerobic bottles were seeded with a bacterial inoculum from a primary effluent. TCE as well as the other compounds under study (PCE, chloroform, bromidichloromethane and dibromchloromethane) were not degraded under aerobic conditions following incubation for up to 25 week at 25C. There was a slight decrease in TCE and PCE concentration under anaerobic incubation for up to 16 weeks. Subsequent batch and continuous flow column studies of TCE degradation in the presence of methanogenic bacteria, showed once again that TCE was slowly biodegraded as compared to tetrachloroethene, carbon tetrachloride or 1,1,1-trichloroethane. In these experiments, acetate was used as a primary substrate and 1- and 2-carbon halogenated aliphatic compounds were used as secondary substrates at relatively low concentrations (<100 ug/L). In both batch and column studies tetrachloroethene (PCE) was transformed to trichloroethene via reductive dehalogenation (Reference 98). Further experiments were undertaken by Vogel and

McCarty (Reference 99) who studied PCE and TCE degradation in small and large glass beads columns under anaerobic conditions with detention times of 2 and 6 days, respectively. More than 99.98 percent of the labeled PCE was removed following passage through the large columns and up to 73 percent of PCE was transformed to TCE. The authors also observed the formation of dichloroethylene (DCE) and vinyl chloride (VC). Vinyl chloride increased to 290 ug/L following 10 days of operation. Figure 9 shows the degradation products of PCE. Under similar experimental conditions, ethylene dibromide ($BrCH_2CH_2Br$) is also biotransformed in the presence of methanogenic bacteria to a highly volatile hydrocarbon probably ethylene (Reference 100).

Wilson et al. (Reference 101) studied the aerobic degradation of TCE, PCE and other compounds in actual aquifer materials (depth = 2.1 - 4.8m) from two sites in Oklahoma and Louisiana. No detectable biological degradation of TCE and PCE was observed under the experimental conditions used. Since degradation was noted in autoclaved samples, the authors postulated that TCE and PCE degradation was likely due to abiotic processes. The abiotic degradation rates were similar to those observed by Dilling et al. (Reference 34). These results confirm those of Bouwer et al. (Reference 97) who found no degradation of TCE under aerobic conditions. Thus, the biological transformation of TCE was thought to be possible under anaerobic conditions (Reference 101).

Vinyl chloride as well as cis- and trans-1,2-dichloroethene have been detected in groundwater in Florida (Reference 102). Vinyl chloride was also found in the source water (groundwater) drawn by 18 out of 34 water treatment plants in Florida (Reference 103). These

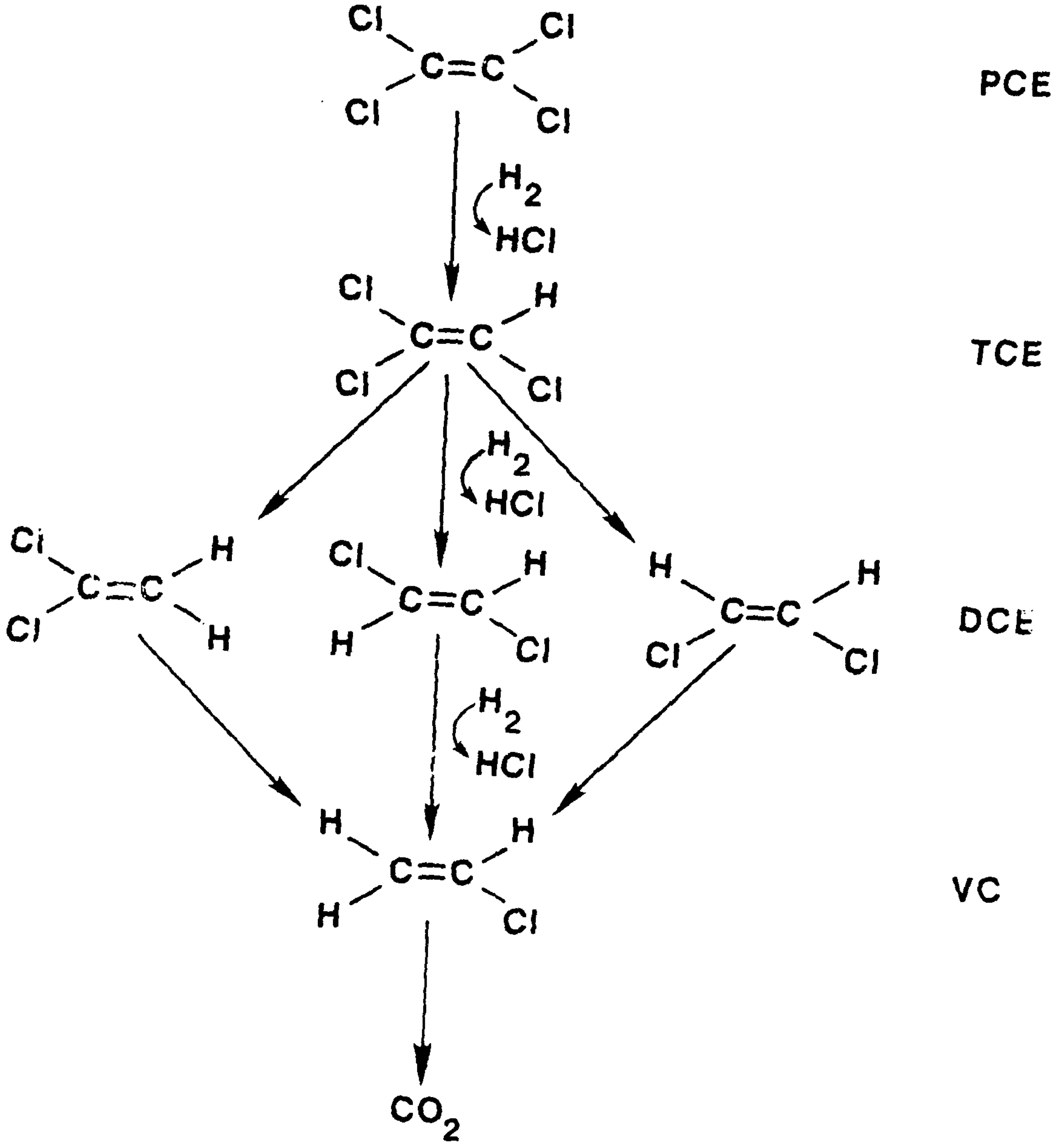


Figure 9. Schematic for Possible Pathway for Conversion of PCE to CO_2 through Reductive Dehalogenation (Reference 99)

finding have led Parsons and her collaborators (Reference 104, 105, 106) to investigate the fate of PCE and TCE in muck. In south Florida groundwater is withdrawn from the Biscayne Aquifer, a shallow aquifer composed of porous calcereous materials. In some areas, surface water is continuous with groundwater and enters the subsurface environment through a muck bed (Reference 104). This explains why muck was used in degradation experiments undertaken under anaerobic conditions. These laboratory experiments have demonstrated that PCE was biotransformed to TCE under presumably (the dissolved oxygen content in the bottles was not measured and no redox indicator was used) anaerobic conditions. Cis and trans 1,2-dichloroethene, dichloromethane and chloroethene were detected following 21-day incubation. These compounds were detected in groundwater at a TCE spill site in Vero Beach, Fla. (Reference 104). However, vinyl chloride formation does not occur in all the microcosms under study. This compound was found in only 3 out of 24 microcosm spiked with TCE. It was also observed that the cis isomer of 1,2-dichloroethene occured at higher concentration that the trans isomer (Reference 105). Another study (Reference 106) once again demonstrated the biodegradation of TCE following an 18-month incubation at 25°C (TCE was reduced from 2.3 mg/L to 0.2 mg/L). Traces of vinyl chloride (6 ug/L) were detected only after 18 months. Lage and Parsons (Reference 70) used the same muck sediment to study the biotransformation of 1,1-dichloroethene, cis-1,1-dichloroethene and trans-1,2-dichloroethene. All the compounds were degraded to vinyl chloride following a 6-month incubation at 25C in the absence of oxygen. They observed that the cis isomer of 1,2-dichloroethene displayed a transformation pattern different from that of trans-1,2-dichloroethene. Chloroethane was found as a degradation byproduct of cis-1,2-DCE in addition to vinyl chloride. It is worth adding that the microorganisms involved in the transformations discussed above are soil and aquatic microorganisms from surface waters and not "true" subsurface microorganisms.

Trichloroethene is, thus, biodegraded under anaerobic conditions and the mechanism involved is probably reductive dehalogenation. This process consists of the replacement of the halogen with hydrogen (Reference 98). It involves the transfer of electrons from a reduced organic compound to the halogenated hydrocarbon (see Figure 10). The mediator involved in electron transfer may be a microorganism, iron or a biological catalyst (e.g., prophyrins, flavins, cytochromes...) (Reference 94, 107). Reductive dehalogenation operates in the transformation of insecticides (References 108 and 109). Anaerobic conditions occur in subsurface environments and the presence of methanogenic bacteria with subsequent methane formation have been documented in groundwater. Leenheer et al. (Reference 110) reported the formation of methane gas following deep-well injection of organic wastes. Two methanogenic bacteria (Methanobacterium and Methanococcus) were isolated from groundwater when methane was present (Reference 111). Another methanogenic bacterium, Methanobacterium bryantii, was isolated from a deep aquifer (657-673 m) in Palm Beach, Florida. Methanogenic bacteria with the subsequent formation of methane (< 0.1-21 mg/L) were also involved in the degradation of phenolic compounds (Reference 112). Thus, the conditions exist for the anaerobic degradation of trichloroethene in specific subsurface environments.

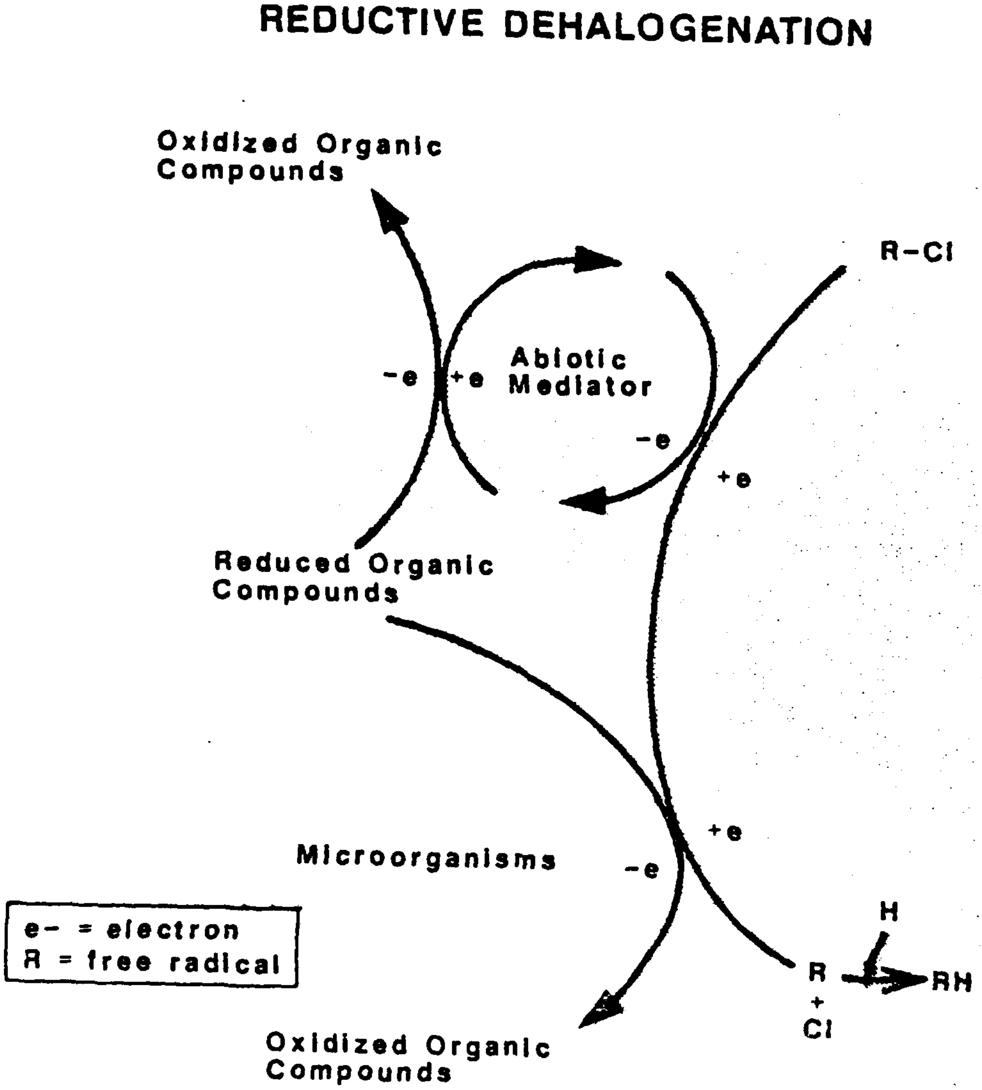


Figure 10. Reductive Dehalogenation (Reference 94)

B. CONCLUSIONS ON BIODEGRADATION

Our review on the microbial degradation of trichloroethene resulted in following conclusions:

1. Trichoroethylene is an important groundwater contaminant and was found to be relatively persistent under field conditions.

2. Under laboratory conditions, trichloroethene is slowly biodegraded as compared to other chlorinated hydrocarbons. This confirms the finding under field conditions.

3. Continuous-flow studies, using glass beads, have shown that TCE is biodegraded under anaerobic conditions in the presence of methanogenic bacteria. These findings have been confirmed by biodegradation studies with actual aquifer material.

4. In soils, TCE is also biodegraded under anaerobic conditions. However, when the soil is treated with natural gas, TCE is transformed under aerobic conditions by presumably methylotrophic bacteria.

5. The anaerobic biodegradation by-products of TCE are 1,2-dichloroethene (cis- and trans-isomers) and vinyl chloride, a human carcinogen.

6. Anaerobic biodegradation of TCE operates via reductive dehalogenation.

7. More studies are needed to investigate these findings under field situation. The oxidation of TCE by methylotrophs and more specifically by methanotrophs is of great interest and this phenomenon should be investigated under <u>in situ</u> conditions. The use of methane gas as a source of carbon and energy for methanotrophs is a possibility.

8. The microorganisms involved in the degradation of TCE should

be identified. It should be determined whether isolated microbial species or microbial consortia are responsible for the biodegradation process.

SECTION VIII

ENVIRONMENT: SITE FOR DEGRADATION

The purpose of this discussion is to briefly identify some of the key factors in various environmental compartments which will influence rate and modes of TCE degradation. Emphasis is placed on the subsurface environment according to the goals of this study.

A. ATMOSPHERE

Solar radiation provides energy to drive a number of photochemical reactions, including degradation of TCE. The more common reactions are initiated by the short-wave component of sunlight. Reactivity is evaluated by direct photolysis or attack by photochemically reactive species.

Reactive species may include ozone and a variety of radical species (Reference 113). Atmospheric degradation has been determined to be a dominant mode for attenuation of TCE in the environment because of its high vapor pressure and atmospheric breakdown rates.

B. SURFACE WATER

Hydrolysis of dilute solutions of contaminants is a possible mode of attenuation for many compounds. Convection contributes to additional losses from volatilization, and, in surface waters, the rate of loss from volatilization exceeds values for hydrolysis of TCE.

Light-induced transformations have been studied for a number of compounds. Aquatic humic compounds can sensitize photoreactions by triplet energy transfer forming peroxides and/or singlet oxygen. Nitrate, iron species, and peroxides may be responsible for sunlight - initiated free radical oxidations of pollutants in some natural waters (Reference 114).

The predominant effect of suspended solids is to slow reactions due to light attenuation, although the presence of a semiconducting substance such as TiO_2 can photocatalyze decompositions (Reference 115).

C. SOIL-ATMOSPHERE INTERFACE

The soil-atmosphere interface is expected to attenuate concentrations of many pollutants. In addition to volatilization to the atmosphere, this area has greater biological activity than other compartments and photoinduced reactions are feasible.

Light is very effective in transforming organic chemicals adsorbed on solids, possible inducing complex reactions catalyzed by trace substances. Adsorption may bring about bathochromic shifts. Hautala (Reference 116) found that photochemistry on soil surfaces is less efficient than the corresponding photochemistry in aqueous solution.

Again, due to convection and direct exposure to air, volatilization would be expected to be a dominant fate mechanism.

D. VADOSE ZONE

Much of the research done on degradation in this zone has been on pesticides. The lack of light to provide energy to drive reactions may decrease rates of transformation in this zone.

In areas where solvent spills occur, contaminants may be present in a number of forms: 1) pockets of pure solvent in contact with soil, 2) dilute aqueous solution, and 3) gas phase in contact with solid and/or soil moisture.

Oxygen is typically present in the unsaturated zone, although overall concentrations tend to decrease with depth. This is primarily attributed to oxygen uptake during biological activity near the surface. Anaerobic microenvironments are expected in localized areas (Reference 118). Both chemical and microbial degradation are affected by factors such as cation exchange capacity, organic matter content, moisture, temperature, aeration, and soil composition.

Redox potential falls to extremely low values in an anaerobic system and oxidation-reduction potentials as low as -650 mV have been measured (Reference 119).

Due to the high ratio of solid to liquid, heterogeneous reactions or surface-catalyzed reactions have been studied particularly in relation to pesticide degradation.

According to Plimmer (Reference 119) "Free radicals are present in soil. Some of these are associated with the humic acid fractions. It has been proposed that their formation and properties are intimately associated with the nature of the silicate environment, since the EPR signal widths vary widely in humic impurities found in different clay types. Other soil components such as lignins, tannins, resins, pigments and antibiotics contain free-radical species. ...The role of free radicals in soils remains to be established. They inhibit one-electron metabolic processes, scavenge halogen-containing compounds or catalyze polymerization reactions."

The main properties of mineral surfaces relevant to their catalytic ability are source and quantity of their surface charge, the nature of the exchangeable cation, and the hydration status of the surface. Changes in moisture content may affect both the phase distribution and properties of the solid-liquid interface. At low moisture content, the pH at the solid-liquid interface may be several units lower than in the bulk solution (Reference 120).

The nature of the clay can affect degradation rate and degradation mechanisms. For example, parathion isomerizes on bentonite surfaces and hydrolyzes on kaolinite as primary pathways. Studies of catalytic behavior show different effects with air dried versus oven dried clay as well as specific pesticide-clay interaction. The mechanisms are not clearly understood making, it difficult to generalize or predict behavior of other contaminants on a specific clay surface (Reference 121).

The nature of the exchangeable cation could affect catalytic activity. Dieldrin degradation by homoionic kaolinite decreased in the order: Al = H>Ca>Na, while for parathion: Ca>Na>Al. The order for homoionic bentonite degradation of ronnel was Al>Fe>H>Mg>Ca.

Catalytic activity is affected by moisture content, and free water may decrease the importance of surface-catalyzed reactions.

References did not address possible gas-phase reactions, or anhydrous reactions between solvents and solid surfaces. Rates of volatilization may be limited by diffusion processes, however, the roles of other modes of attenuation have not been evaluated.

E. GROUNDWATER

Where large quantities of solvents reach the groundwater, the contaminant may be in excess of solubility of water and the aquifer will have multiple phases. Attenuation for dilute aqueous solutions of contaminants must also be addressed.

Common cations and anions include calcium, magnesium, sodium, bicarbonate, sulfate, and chloride. The pH typically ranges from 6-8.

Oxygen levels are limited as compared to the vadose zone although very few studies of dissolved oxygen have been reported in the literature. Even with loss of oxygen the redox level may be relatively high. The electrochemical sequence of reduction indicates consumption of oxygen is followed by reduction of NO_3 and MnO_2, ferric iron minerals, and when sufficiently negative redox levels are reached SO_4 is reduced with reduction of organics to methane and CO_2. Most of these reactions are biologically mediated (Reference 122).

Although methane is produced in some groundwater, it is common for groundwater not to evolve to conditions of low redox potential. Redox reactions may not proceed due to low concentrations of the necessary bacterial populations. These populations may be limited by availability of organic substrates or nutrients.

Many of the interactions between contaminants and soils characteristic of the vadose zone may also play a role in attenuation of pollutants in groundwater.

SECTION IX

CONCLUSIONS

Very little information is known about potential abiotic degradation of TCE in subsurface environments. The reaction which is typically easiest to characterize is hydrolysis. There is considerable uncertainty regarding the mechanism of loss of TCE in aerobic aqueous systems. Products have not been identified, and it is unclear if the reaction occurs with water, oxygen, or both of these compounds. The half-life for TCE "hydrolysis" was estimated to be at 10.7 months, in studies performed at pH 7.

The potential importance of this reaction depends on whether this rate is competitive with other attenuation mechanisms and also if it is possible to accelerate the reaction. The dominant competing fate mechanisms are volatilization and biodegradation.

Rates of diffusion of contaminants in the subsurface limit losses typically attributed to volatilization and subsequent photoxidation in the troposphere. In surface water systems, convection assists in promoting the volatilization process. When upward gradients are not present in the zone of contaminated groundwater, the potential loss from the surface of the water table depends primarily on the rate of diffusion to the surface. The diffusion coefficient used in modeling studies for TCE in saturated soils is 4.12×10^{-6} cm^2/s. To illustrate, assume a plume containing 100 ppm of TCE is present 5 meters below the surface of the water table and the only way it can reach the surface to volatilize is by diffusion. After 1 year, the concentration which has reached a distance of 1/2 meter above the plume via diffusion will be less than 0.25 ppm.

Biodegradation is considered a dominant method for transforming chemicals in soil, particularly in the upper zone. Degradation by microbes will occur deeper in the vadose zone and groundwater, although rates are significantly slower due to typically smaller populations of microbes. Populations are limited by availability of a carbon source, nutrients, and/or oxygen. In areas where these factors are not limited, higher rates of degradation occur. Enhanced rates of degradation are produced with addition of limiting factors to achieve bioreclamation of contaminated soils or aquifers.

Anaerobic degradation products of TCE have been observed in numerous sites. Compounds resulting from dehalogenation reactions appear typically in areas where a separate carbon source is available to enhance microbial populations, lower the redox potential, and cometabolize the TCE. Examples of reducing environments include areas with large amounts of organic matter in the soils (muck), municipal landfills, and sites with a variety of nonchlorinated organic compounds which may serve as a carbon source for cometabolism. The cis-DCE and vinyl chloride products formed under these conditions are resistant to further degradation and create health risks greater than those posed by TCE.

Trichloroethene contamination in less reducing environments may be more persistent. Aerobic degradation of TCE may be restricted to microorganisms which contain monoxygenase enzyme systems. Although these are ubiquitous, concentrations would typically be low.

Measurements of rates of TCE degradation in aerobic groundwaters correlated with rates of hydrolysis measured by Dilling et al. (Reference 34). The losses were assumed to be due to abiotic processes. It is under these conditions, where volatilization is restricted and biodegradation is limited by low microbial populations in aerobic groundwaters, that abiotic degradation attributed to loss by hydrolysis creates greater interest.

Free radicals react with TCE. If large excess energy sources like those in the troposphere are not present, the principal mode of attack is addition to the double bond at the carbon which contains the hydrogen. Condensation would be more expected than a polymerization reaction. In the subsurface where pockets of pure solvent may be present, a chain reaction may be sustained once it is initiated. The reactions presented in this report illustrate the mode of attack, however, information on types and concentrations of free radicals which may be present in these subsurface environments have not been identified. The importance of this attenuation mechanism therefore, is unclear.

Autoxidation may occur particularly in the vadose zone in areas where spills have occurred an molecular oxygen is present. This reaction may not require a free radical initiator, however, this process would be accelerated if free radicals were present. Soil surfaces may help to initiate this type of reaction by providing a polarizing surface. These surfaces may also promote gas-phase reactions.

Trichloroethene has been shown to undergo elimination in the gas phase above an aqueous solution of pH 11. The dichloroacetylene formed in this reaction may be more readily formed in the gas phase, since a simultaneous substitution reaction may occur in the aqueous phase. Whether this base catalyzed reaction will occur at pH ranges more typical of the subsurface has not been established. The high reactivity of DCA may result in formation of other intermediates.

Nucleophilic substitutions have been demonstrated for TCE, primarily under base-catalyzed conditions. Whether this could be extended to possible environmental reactions depends on the potential for the elimination reaction to occur. If elimination occurs, the most probable loss of the DCA would be reaction with oxygen. A mechanism other than elimination-addition may occur under the milder conditions encountered in the environment. This has not been demonstrated.

Nucleophiles which may be present in the subsurface have not been fully described. Nucleophilic attack by sulfide on chlorinated alkanes has been demonstrated. The rates were competitive with hydrolysis, which reflects the compounds potential reactivity with a nucleophile. Unfortunately, since a similar reaction has not been demonstrated for TCE and the rate of "hydrolysis" may reflect a reaction with oxygen, it is not possible to project reactivities with nucleophiles like sulfides under environmental conditions.

Trichloroethene can be biologically and chemically reduced to dichloroethenes (primarily the cis isomer) and vinyl chloride. This reaction does not appears to be of great interest to organic chemists and very little information was available to project mechanisms and rates, particularly in an aqueous environment. Studies of chemical reduction reactions in the environment typically include the use of reagent, enzymes and/or cell extracts which may play a role in electron transfer reactions. Studies of chemical transfer hydrogenation typically use organic hydrogen donor compounds which may be present in an anaerobic environment. The roles of these compounds in the reduction of TCE have not been evaluated.

SECTION X

RECOMMENDATIONS

A. BASIC RESEARCH NEEDS

In addition to enhancing our understanding of the potential behavior of a particular contaminant, environmental conditions must be better understood. The complexity of the subsurface environment makes it difficult to generalize about behavior of chemicals in that zone, however continued research in this area will allow us to establish patterns and make predictions about potential reactivity.

Continued attention should be given to a basic understanding of the subsurface environment and chemical reactivity and mechanisms. Particular topics which would provide better understanding of the behavior of TCE include:

1. Free Radicals in Subsurface Environments

Since TCE is susceptible to attack by free radicals, it is important to determine if free radicals are present in the vadose zone or groundwater environments. Plimmer (Reference 119) states free radicals are present in soil, however, it is not clear if this is a surface phenomenon and the details of the experiments were not available.

If free radicals are present under specific conditions, it is necessary to clarify the expected concentration and the nature of the radical species.

This mode of attenuation of TCE is likely to be most important in cases where the solvent concentration is high and multiple phases are present. Reactions would be sustained more readily in the gas or liquid solvent phases, rather than dilute aqueous solution.

2. Soil Catalysis

An increasing amount of attention is being paid to catalysis by clays in conditions resembling the natural environment. Increases in rates of abiotic degradation may be caused by pH effects or interaction with specific minerals which may be present on the surfaces.

A possible approach to assist in understanding potential abiotic degradation of TCE is to focus on conditions likely to promote formation of a carbanion or an elimination reaction. Reactivity over polar zeolite catalysts and the roles of acidic/basic sites and promotion of the elimination by specific elements can be evaluated.

Aluminum has been determined to increase reactivity of TCE under specific conditions. Whether exposed aluminum on the edges of minerals in contact with the liquid solvent phase of TCE would show similar reactivity is another question to be answered.

3. Mechanisms of Autoxidation and Reduction

Lack of information on the specific requirements for these reactions hampers our ability to predict reactivity.

It is important to clarify whether autoxidation of TCE occurs in the absence of free radical conditions. Under conditions of multiple phase flow it may be possible to sustain a reaction once it is initiated between oxygen and the liquid solvent phase.

Difficulties have been encountered in determining mechanisms of reduction reactions. Various catalysts are used for specificity in organic synthesis reactions, to reduce one functional group in the presence of another. The catalysts are not expected to be present in the environment so one can neither select an adequate alternative nor decide if the catalyst is essential for the reaction to occur.

Compounds like TCE appear to be easily reduced; however, it is necessary to examine the minimum conditions required for that reaction to occur under environmental conditions rather than for an industrial or organic synthesis application.

B. ABIOTIC DEGRADATION OF TCE IN SOILS AND GROUNDWATER

We strongly recommend a reexamination of the hydrolysis of TCE, particularly establishing the kinetics of a possible base-catalyzed reaction. In addition, we propose additional evaluation of chemical reduction which may mimic environmental conditions. Both of these topics would provide clarification of kinetics involved with reactions which are known to occur and provide insight into possible treatment mechanisms.

1. Base-Catalyzed Hydrolysis and/or Oxidation

There are three main reasons to investigate the kinetics and conditions for the reactivity of TCE in mild alkaline solution:

a. Under specific site conditions the rate of attenuation by this mechanism may be competitive with other modes of loss.

b. The potential for side reactions to occur may depend on the rate of formation of carbanion.

c. Techniques for enhancing this effect may provide a possible treatment mechanism.

The investigation should examine the rate of loss of TCE in buffered aqueous solutions at various pH levels. Experiments should be conducted in the dark to avoid production of free radicals via radiation which would not be present in the subsurface.

The role of oxygen may be determined by evaluating the rate of degradation and products formed in the presence and absence of dissolved oxygen in the buffered solutions. Under basic conditions, acetylenes which may be formed could form peroxides upon contact with oxygen. This may induce other reactions. The TCE used in these experiments should not therefore contain inhibitors.

Most products may be analyzed by gas chromatography/mass spectroscopy (GC/MS). Radiolabled TCE may be required to elucidate a mechanism or to determine transformation of CO_2.

The rate of deuterium exchange in an alkaline aqueous solution would assist in determining if the carbanion plays a vital role in the reactivity of TCE.

These experiments should also be conducted on other halogenated olefins in the series: tetrachloroethene, dichloroethene isomers, and vinyl chloride. Differences in reactivity among these compounds will assist in pointing to a mechanism and will provide necessary information for evaluating effects of a change in environment on the loss of these compounds.

2. Reduction

Many compounds, including TCE, are thought to be at least partially abiotically reduced. Many of the compounds used in studies of homogeneous transfer hydrogenation as organic hydrogen donor molecules are present in anaerobic biologically active environments. We recommend exploring the behavior of TCE in anaerobic aqueous systems in the presence of reducing agents.

The approach to the study would include an initial survey of reducing agents commonly used in industry or organic synthesis appropriate for use in an aqueous system. Rates and products should be determined and the need for catalysts evaluated.

The second phase would include assessing reduction under more mild conditions and selecting organic donor molecules and catalysts which are likely to be present in anaerobic environments. The possible catalytic action of natural soils could also be tested.

Again, these tests must be performed on the homologous series since reactivity is expected to vary and will help to establish an understanding of the mode of reduction.

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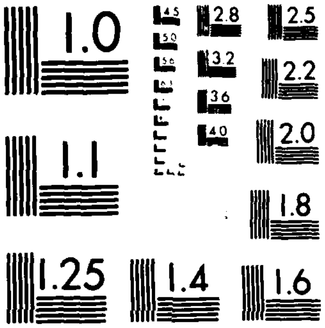

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APPENDIX A

Summary of Free Radical Reactions of TCE

Conditions: UV illuminated titanium dioxide, dilute aqueous solution
Primary Products: Hydrogen chloride, Carbon dioxide, dichloroacetaldehyde
Reference: 80 Pruden and Ollis 1983

Conditions: TCE + Isobutene; 500°C Gas phase
Primary Products: 1,1-Dihalogeno-4-methylpenta-1,4-dienes
Reference: 47 Hewertson et al. 1978

Conditions: TCE + Isobutene, 500°C Gas phase, Organic peroxides
Primary Products: 1,1-dihalogeno-4-methylpenta-1,4-dienes
2,5-Dimethyl hexadienes
Reference: 55 Holland et al. 1979

Conditions: TCE + Cyclohexane; 27-150°C
γirradiation, liquid solvent solution
Primary Products: Cyclohexyl dichloroethylene, hydrogen chloride
Reference: 42, 43 Horowitz and Rajbenbach 1969, 1973

Conditions: TCE + Cyclohexane + Carbon tetrachloride;
γ-irradiation, 323-448°K, gas phase
Primary Products: Chloroform, chlorocyclohexane
1,1-dichloro-3,3,3-trichloropropene
Reference: 44 Horowitz and Baruch 1980

Conditions: TCE + triethyl silane
γ-irradiation, 65°C, liquid phase
Primary Products: Cis + Trans-dichloroethylene, Triethylchlorosilane, dichlorovinyltriethylsilane, hydrogen chloride
Reference: 67 Aloni et al. 1979

Conditions: TCE + olefins; t-Bu$_2$O$_2$
130-140°C, liquid solvent phase

Reference: 36 Guy and Pearson 1977

Conditions: TCE + vinylchloride, 40-60°C, ammonium persulfate + sodium bisulfite, autoclave

Primary Products: Copolymer

Reference: 21 Kirk and Othmer 1964

Conditions: Photooxidations: chlorine, mercury, ozone, or atomic oxygen. Gas phase, radiation

Primary Products: Carbon dioxide, carbon monoxide, dichloro acetyl chloride, phosgene, hydrogen chloride, chloroform

Reference: 52 Sanhueza et al. 1976

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