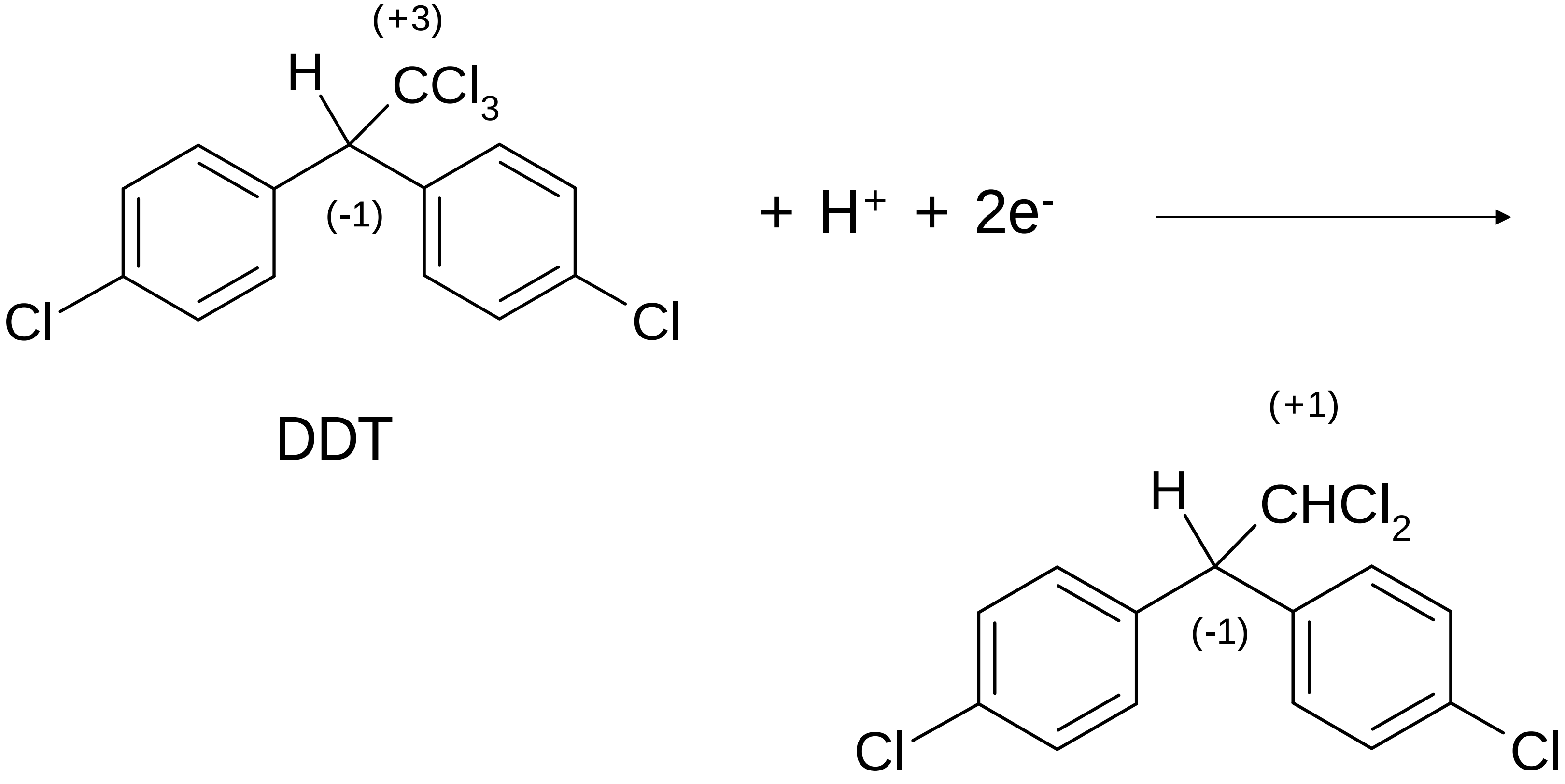
Net electron transfer



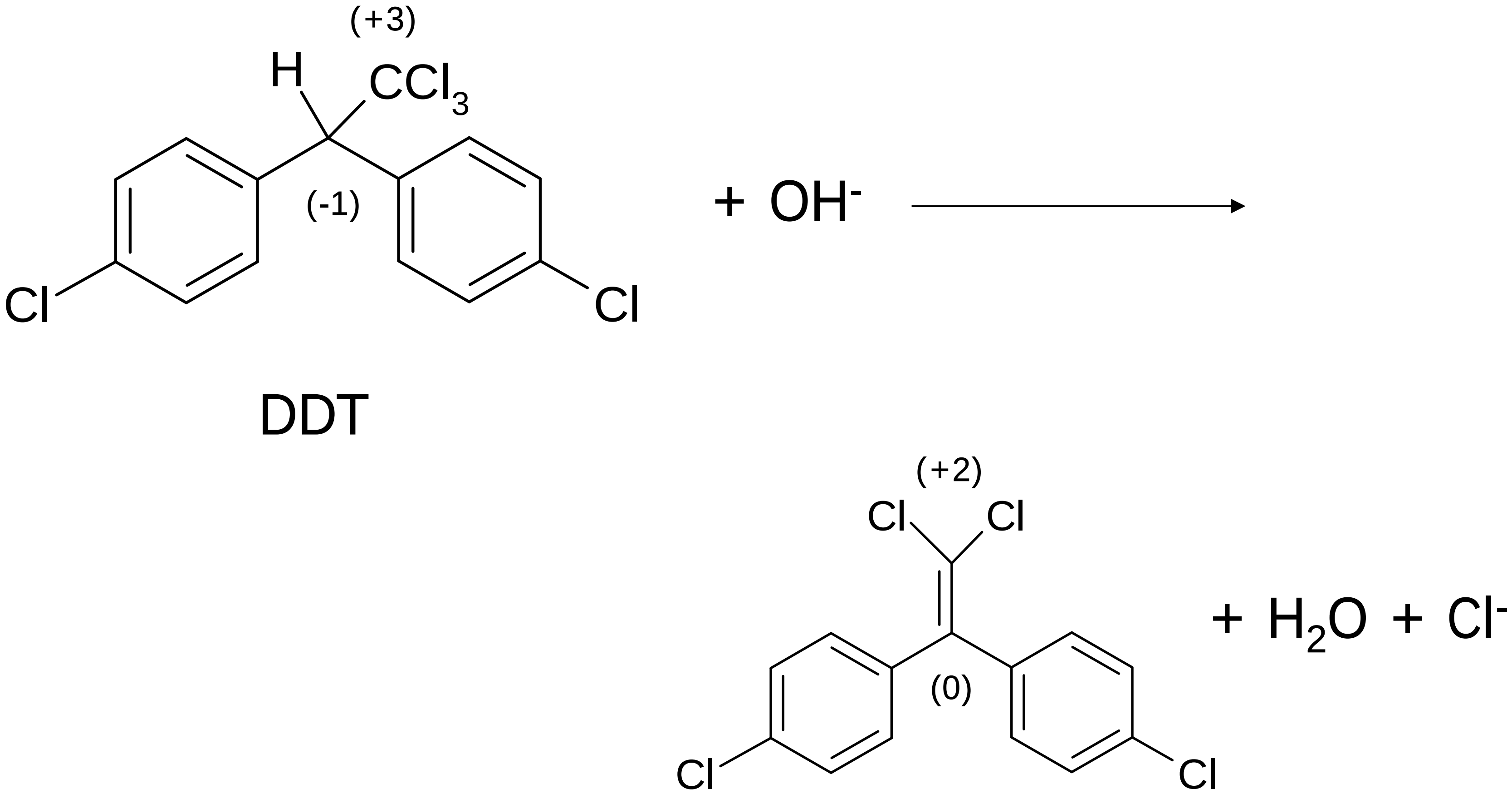
DDT

$+ H^+ + 2e^-$

DDD

Reductive dechlorination

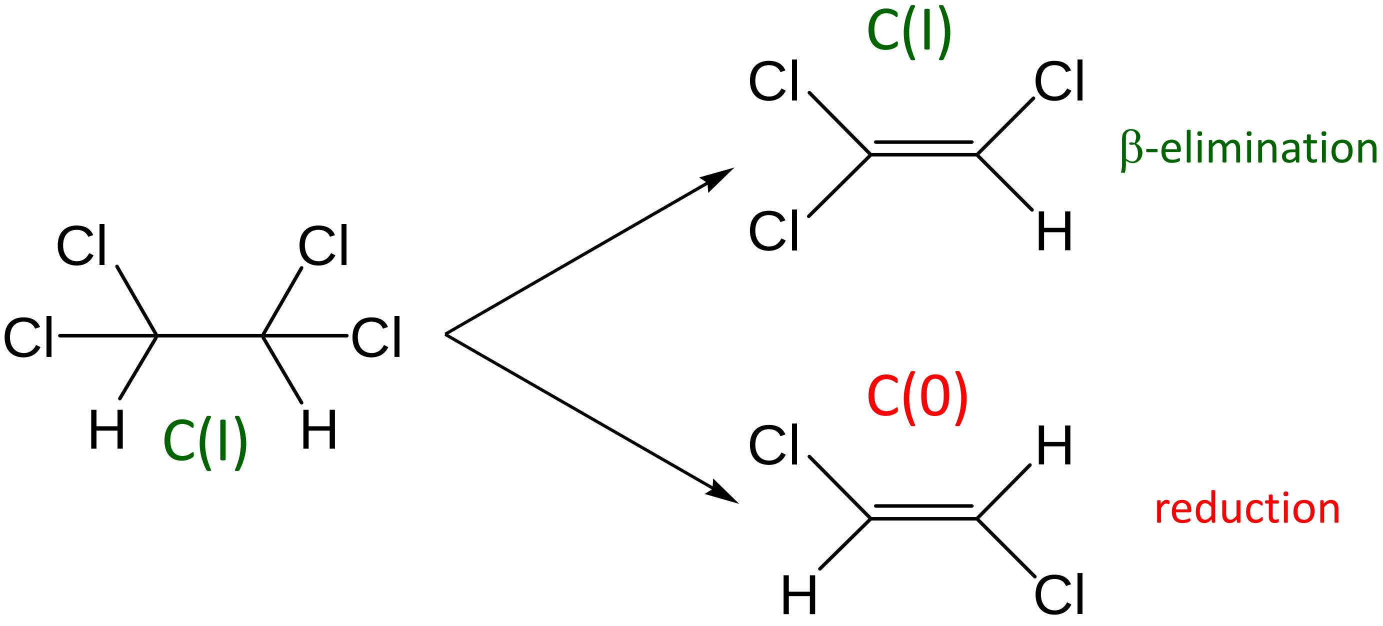
NO net electron transfer

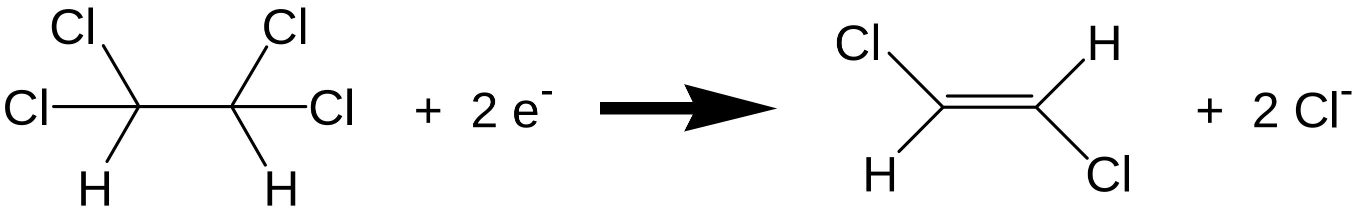


DDT

DDE

Elimination (dechlorination)



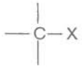
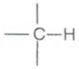
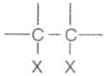
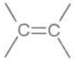
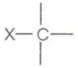
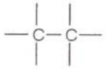
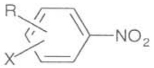
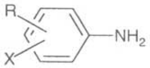
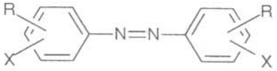
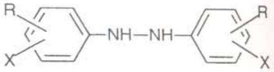
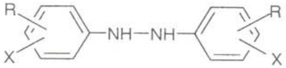
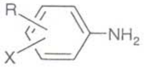
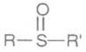


reductive dehalogenation (dihalo-elimination)
half-cell reaction

Redox Reactions

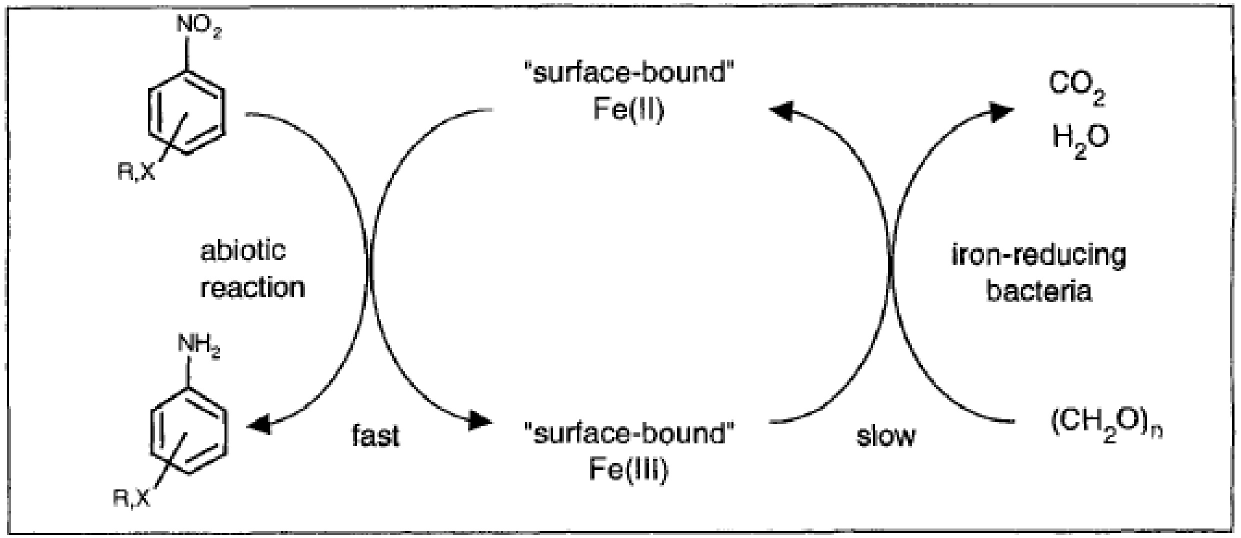
- Redox reaction keys
  - only a few functional groups involved
    - carbon (carboxy, quinone, halo-aliphatics)
    - nitrogen (nitro, amine, azo)
    - sulfur (disulfide, thiol, ..., sulfonate)
  - mechanisms not always clear
    - may be several steps
    - depicted just as electron transfer in half-cell rxn
    - electron donors, acceptors not always known
  - more difficult to determine reaction rates

Table 14.1 Examples of Some Simple Redox Reactions That May Occur Chemically in the Environment [a]

Oxidized Species	Reduction ⇌ Oxidation	Reduced Species	E N
	Change in Oxidation State of Carbon Atom(s)		
R–COOH + 2 H^+ + 2 e^-	←	R–CHO + H_2O	
 + 2 H^+ + 2 e^-	⇌		
 (X=Cl,Br,I) + H^+ + 2e^-	→	 + X^-	
 (X=Cl,Br,I) + 2e^-	→	 + 2 X^-	
2  (X=Cl,Br,I) + 2e^-	→	 + 2 X^-	
	Change in Oxidation State of Nitrogen Atom(s) [b]		
 + 6 H^+ + 6 e^-	⇌	 + 2 H_2O	
 + 2 H^+ + 2 e^-	⇌		
 + 2 H^+ + 2 e^-	⇌	2 	
	Change in Oxidation State of Sulfur Atom(s) [c]		
R–S–S–R + 2 H^+ + 2 e^-	⇌	2 R–SH	
 $R\text{–}\overset{O}{\overset{\parallel}{S}}\text{–}R'$ + 2 H^+ + 2 e^-	⇌	R–S–R' + H_2O	

Redox Kinetics

- Electron transfer mediators



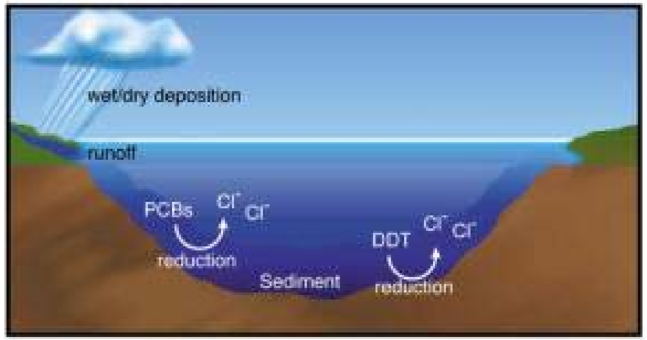
  - variety of compounds
    - transition metal complexes (Fe(II) porphyrin)
    - NAD/NADH; AQDS/AHDS
    - lawsone, juglone
    - natural organic matter

Reduction reactions

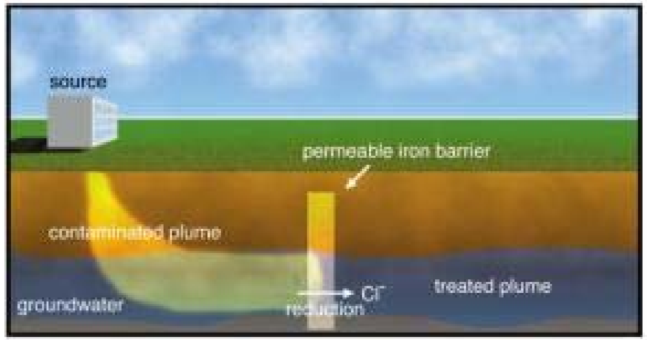
Reduction Reactions

- Catalog of reduction reactions
  - reductive dehalogenation
    - $R—X \leftrightarrow R—H$
    - $R—CHX—CHX—R \leftrightarrow R—CH{=}CH—R$
  - nitroaromatic reduction
    - $Ar—NO_2 \leftrightarrow Ar—NH_2$
  - aromatic azo reduction
    - $Ar\text{-}N{=}N\text{-}Ar \leftrightarrow Ar—NH_2$
  - sulfoxide reduction
    - $R—S({=}O)—R \leftrightarrow R—S—R$
  - quinone reduction
    - $O{=}Ar{=}O \leftrightarrow HO—Ar—OH$
  - reductive dealkylation
    - $R—X—R \leftrightarrow R—X—H$

A.



B.



Reduction Reactions

- Need electron donors for reduction
  - aqueous species
    - H_2S
    - Fe(II)
    - Mn(II)
    - NH_3
  - minerals, etc.
    - sulfide minerals (e.g., pyrite)
    - Fe(II) minerals (e.g., biotite)
    - Fe(0) in remediation

Reduction Reactions

- Reductive dehalogenation: $RX + H^{+} + 2e^{-} \rightleftarrows RH + X^{-}$
  - reducing conditions (anoxic)
    - promote breakdown of R-X, removal of halogens
    - usually, products are less toxic
    - aliphatic (C_1 and C_2) – fast
    - olefinic (R=R-X) – relatively fast
    - aromatic (Ar-X) –slow (e.g., PCBs, chlorinated benzenes)
  - most reductants capable of reducing R-X
    - high redox potentials mean easy to reduce

Reduction Reactions

- Reductive dehalogenation
  - products depend on reductant
  - example: carbon tetrachloride, CCl_4

$$CCl_4 + 2e^- \rightarrow :CCl_3^- + Cl^-$$

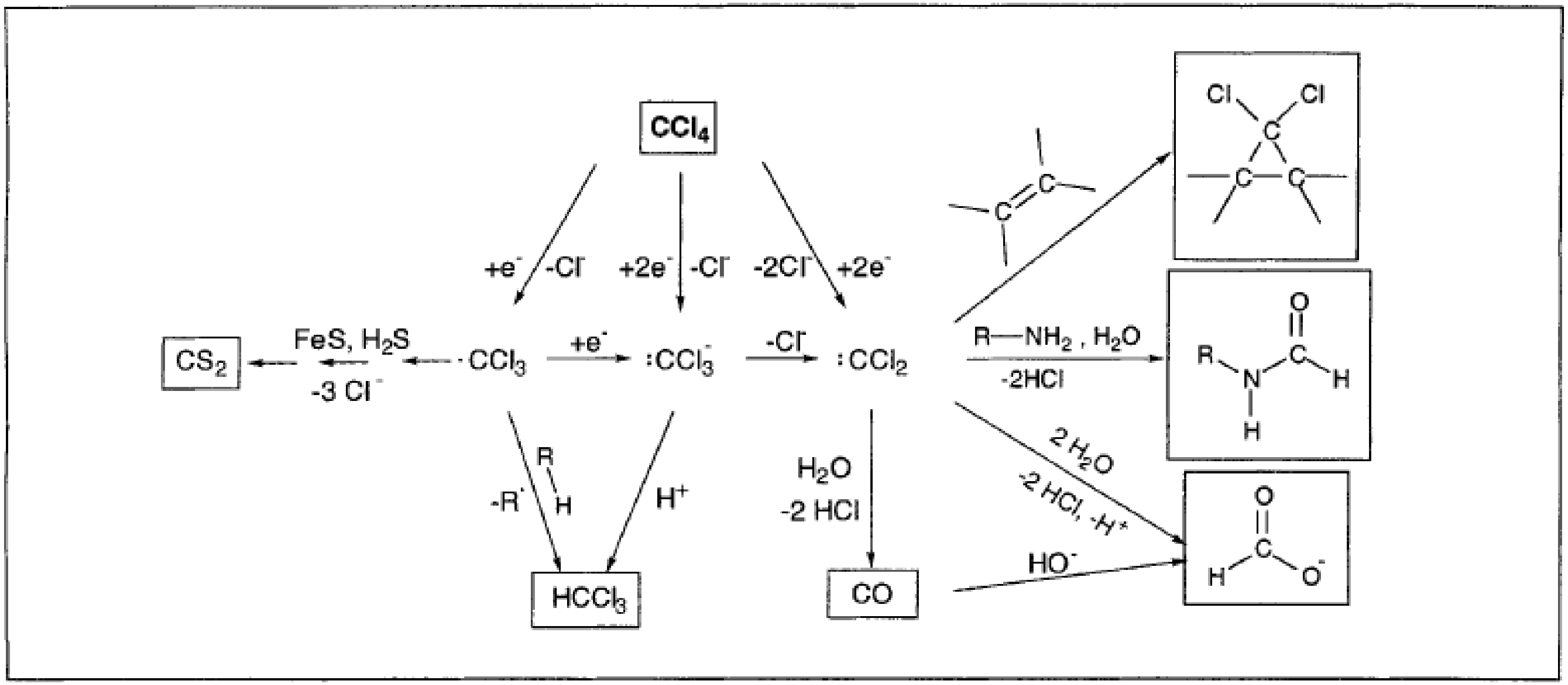
$$:CCl_3^- + H^+ = CHCl_3$$

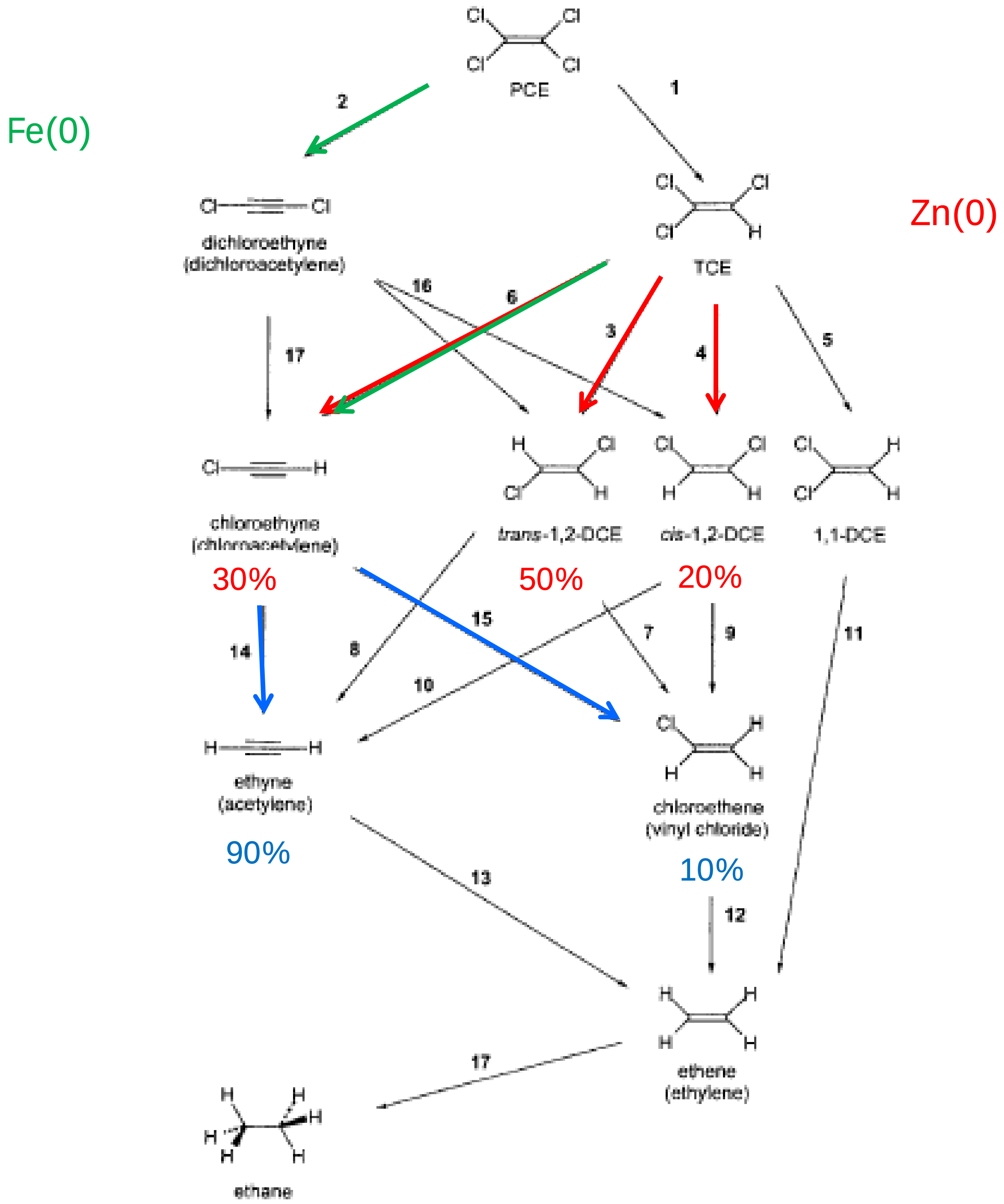
chloroform yield range 10 to 90%

    - two-electron transfer reductant favors chloroform
    - sulfide as reductant ⇒ carbon disulfide

$$CCl_4 + e^- \rightarrow \bullet CCl_3 + Cl^-$$

$$\bullet CCl_3 \xrightarrow{+H_2S} CS_2 + 3Cl^-$$


CCl4
+e- -Cl-
+2e- -Cl-
-2Cl- +2e-
CS2
FeS, H2S
-3 Cl-
·CCl3
+e-
:CCl3-
-Cl-
:CCl2
Cl
Cl
C
C
C
R—NH2 , H2O
-2HCl
O
R
N
C
H
H
2 H2O
-2 HCl, -H+
O
C
H
O-
HO-
R
H
-R·
H+
HCCl3
H2O
-2 HCl
CO


PCE
Fe(0)
Zn(0)
1
2
dichloroethyne (dichloroacetylene)
TCE
16
6
3
4
5
17
chloroethyne (chloroacetylene)
trans-1,2-DCE
cis-1,2-DCE
1,1-DCE
30%
50%
20%
14
8
15
7
9
11
10
ethyne (acetylene)
chloroethene (vinyl chloride)
90%
10%
13
12
17
ethene (ethylene)
ethane

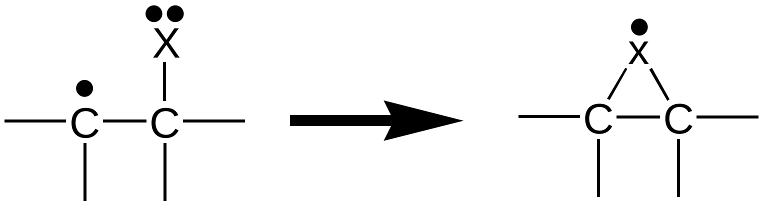
Reduction Reactions

- Reductive dehalogenation
  - rate affected strongly by
    - ease of breaking the C—X bond
      - C—X bond strength
    - stability of carbon radical formed
      - electron-withdrawing substituents stabilize carbon radical

$$CCl_4 + 2e^- \rightarrow \,:CCl_3^- + Cl^-$$

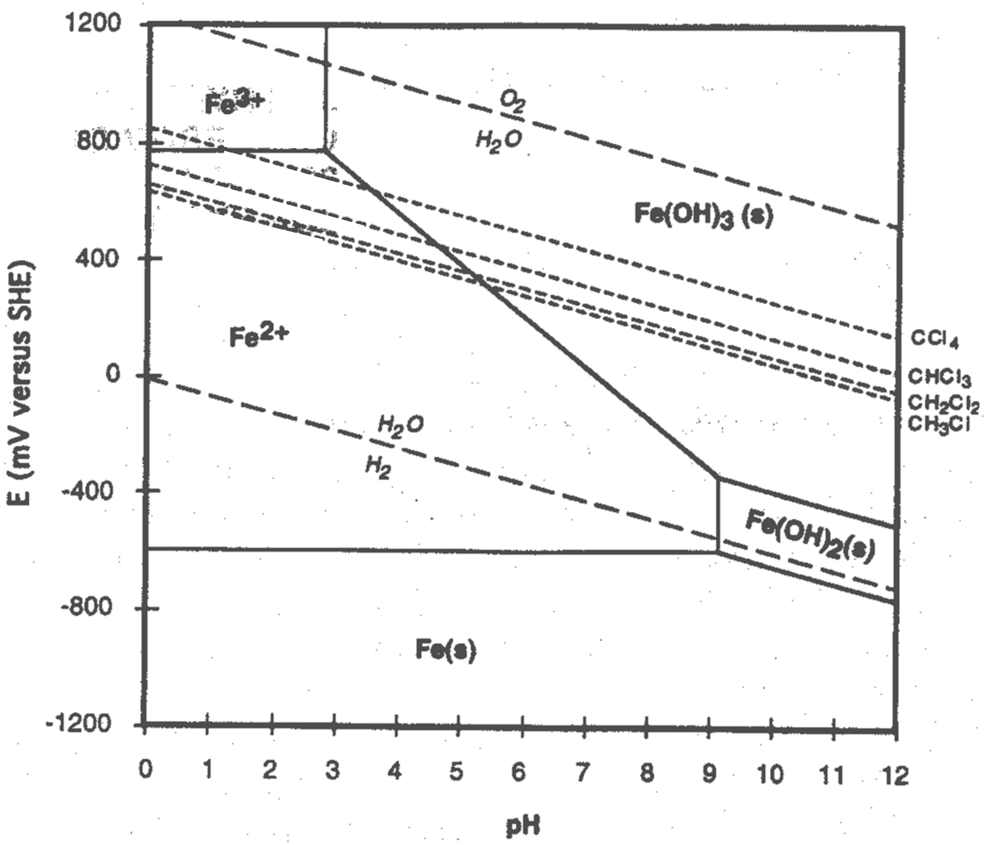
$$:CCl_3^- + H^+ = CHCl_3$$

-
  - rate affected weakly by
    - tendency of C—X to accept electron (electronegativity)
    - stabilization of carbon radical by geminal halogen



Reduction Reactions

- Zero-valent iron
  - permeable reactive barrier remediation
  - other metals also (Sn, Zn, etc.)
  - iron metal is oxidized
    - “rusting”
    - corrosion
  - $Fe^0 = Fe^{2+} + 2\ e^-$
    - $E_H^0(W) \sim -0.6$ V
- Promotes reductive dechlorination



Reduction Reactions

- Permeable reactive barrier

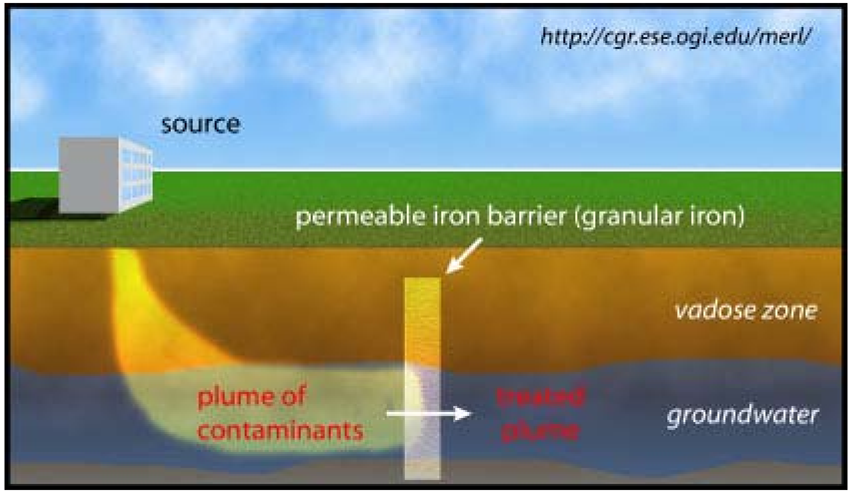


Photo provided by Rocky Flats Environmental Technology Site

Installation of the high-density polyethylene panels at the East Trenches PRB project at Rocky Flats.

  - maintain redox potential (Fe^0 supply)

Oxidation reactions

Oxidation Reactions

- Catalog of oxidation reactions
  - phenol oxidation
    - Ar—OH $\leftrightarrow$ Ar=O
  - aromatic amine oxidation
    - Ar—NH_2 $\leftrightarrow$ Ar—NO_2
  - thiol oxidation
    - R—SH $\leftrightarrow$ R—SO_3^-
  - aldehyde oxidation
    - RC(=O)H $\leftrightarrow$ RC(=O)OH

Oxidation Reactions

- Electron acceptors
  - natural waters
    - oxygen
      - O_2 (actually, the *superoxide* radical)
      - hydroxy radical, peroxide (and peroxy radicals)
    - nitrate
    - Fe(III) and Mn(IV) (aqueous and mineral)
      - Fe(III) oxides, Mn(III,IV) oxides
  - disinfection
    - hypochlorous acid, chloramine, ozone
  - thermal and wet oxidation
    - heat, persulfate, permanganate

Oxidation Reactions

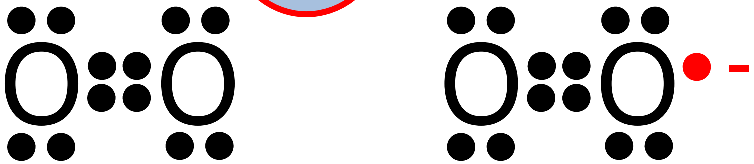
- Oxygen

  $O_2(g) + 4\ H^+ + 4\ e^- = 2\ H_2O \quad E_H^0(W) = 0.81\ V$

  - difficult to accept first electron

    superoxide radical

    $O_2 + e^- = O_2^{\bullet -} \quad E_H^0(W) = -0.16\ V$

  - oxygen not as good an electron acceptor as $E_H^0(W)$ indicates
    - only easily-oxidized compounds oxidized by O_2
      - e.g., thiols, anilines

Oxidation Reactions

- Phenol oxidation by oxides
  - oxidants
    - ferric oxides, oxyhydroxides (Fe(III))
    - manganese oxide, oxyhydroxide (Mn(III/IV))
  - multi-step reaction

"precursor complex" formation: $\equiv Mn^{III}OH + ArOH \rightleftharpoons \equiv Mn^{III}OAr + H_2O$

electron transfer: $\equiv Mn^{III}OAr \rightleftharpoons \equiv Mn^{II} - {}^{\bullet}OAr$

phenoxy radical release: $\equiv Mn^{II} - {}^{\bullet}OAr + H_2O \rightleftharpoons \equiv Mn^{II}OH_2 + {}^{\bullet}OAr$

reduced Mn release: $\equiv Mn^{II}OH_2 \rightleftharpoons Mn^{2+} + H_2O + new\,site$

Oxidation Reactions

- Phenol oxidation
  - half-reaction

    $\mathrm{ArO}^{\bullet} + e^{-} + H^{+} \Leftrightarrow \mathrm{ArOH}$

  - redox potentials valid for ArOH, not ArO^{-}
    - watch pK_a of phenol

$$\equiv Mn^{III}OH + ArOH \rightleftharpoons \equiv Mn^{III}OAr + H_2O$$

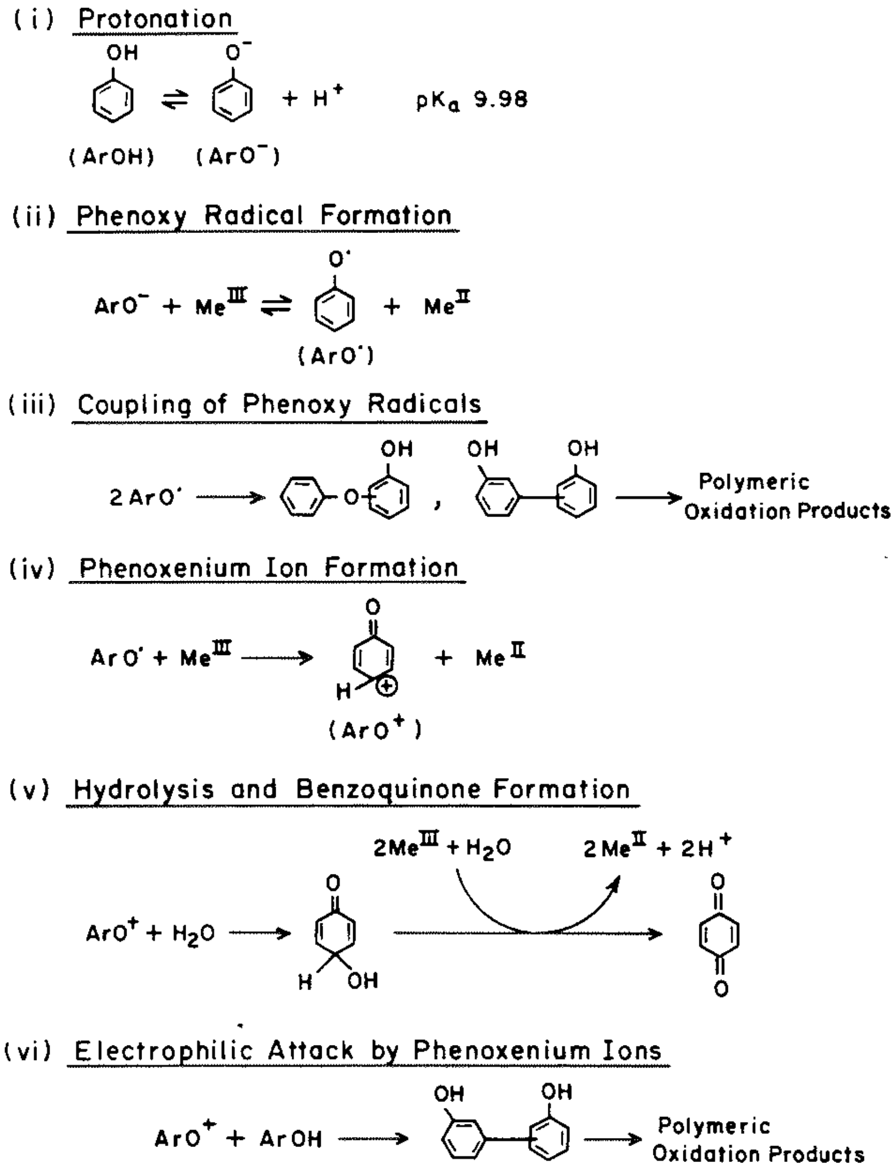
$$\equiv Mn^{III}OAr \rightleftharpoons \equiv Mn^{II} - {}^{\bullet}OAr$$

$$\equiv Mn^{II} - {}^{\bullet}OAr + H_2O \rightleftharpoons \equiv Mn^{II}OH_2 + {}^{\bullet}OAr$$

$$\equiv Mn^{II}OH_2 \rightleftharpoons Mn^{2+} + H_2O + new\,site$$

Oxidation Reactions

- Phenol oxidation
  - fate of the phenoxy radical, ArO•
  - coupling, dimer formation
  - dimers more susceptible to oxidation, leading to polymers



Oxidation Reactions

$$\equiv Mn^{III}OH + ArOH \rightleftharpoons \equiv Mn^{III}OAr + H_2O$$

$$\equiv Mn^{III}OAr \rightleftharpoons \equiv Mn^{II} - {}^{\bullet}OAr$$

$$\equiv Mn^{II} - {}^{\bullet}OAr + H_2O \rightleftharpoons \equiv Mn^{II}OH_2 + {}^{\bullet}OAr$$

$$\equiv Mn^{II}OH_2 \rightleftharpoons Mn^{2+} + H_2O + new\,site$$

- Phenol substituents
  - electron-donating (e.g., -CH_3, -CH_2CH_3)
    - easier to give up electron
    - decreases oxidation potential
    - increases oxidation rate
  - electron-withdrawing (e.g., -NO_2, -Cl)
    - harder to give up electron
    - increases oxidation potential
    - decreases oxidation rate
  - $k_{ox} \propto 1/E_H \propto 1/\Sigma\sigma$ ($\propto k_{diss}$(Mn))

Oxidation Reactions

- Disinfectants = oxidants
  - chlorine (HOCl)
  - chlorine dioxide (ClO_2)
  - chloramines (NH_2Cl)
  - ozone (O_3)
  - activated carbon (surface catalysis)

Oxidation Reactions

- Chlorine (hypochlorite)
  - most chlorine ends up as Cl^-

    $$RCHO + OCl^- = RCOOH + Cl^- + H^+$$

  - some chlorine incorporated in reactants
    - phenol oxidation

Soper and Smith, 1926, *J. Chem. Soc.*, 1582-1591