

13. Chemical Transformation I: Hydrolysis involving other Nucleophilic Species

14. Chemical Transformation II: Redox Rxns

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Reductive Dehalogenation Reactions of Polyhalogenated

C_1 - and C_2 -Compounds

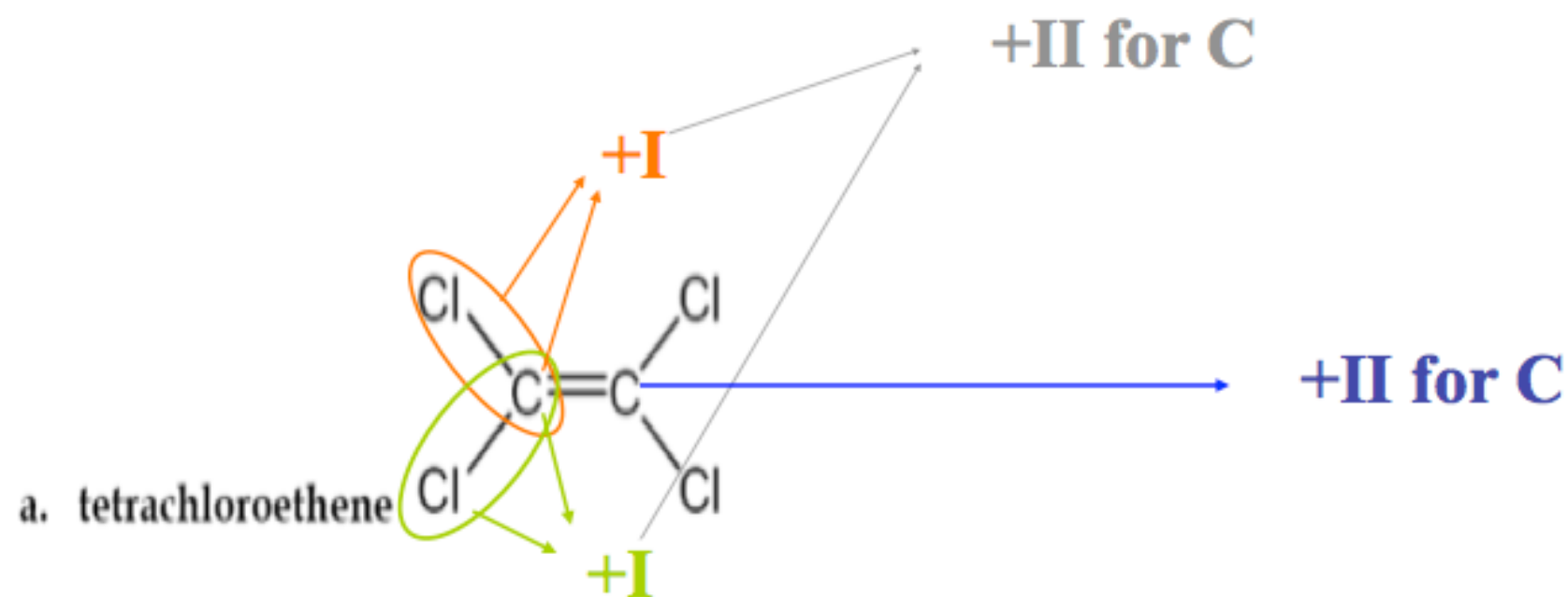
Oxidation Reactions

Big difference is net electron transfer

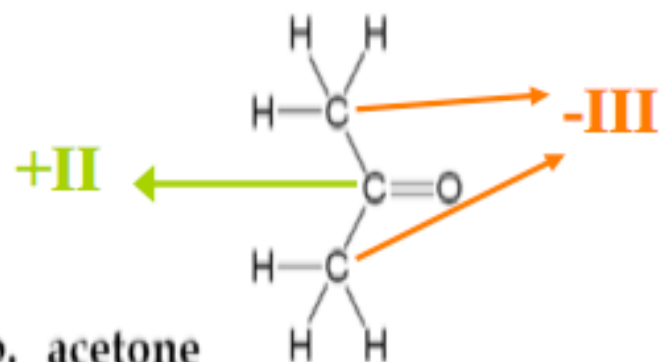
Determination of Oxidation States of Carbon Atoms

Adding

- 0** for each bond to an identical atom
- 1** for each bond to a less electronegative atom
- +1** for each bond to a more electronegative atom



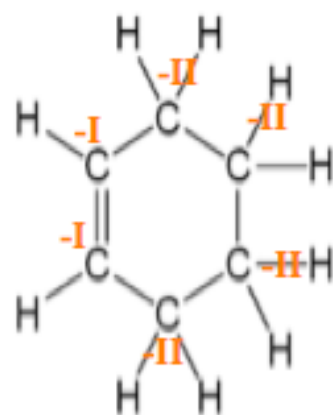
The oxidation state of the first carbon, or the α -carbon, is +II. It loses electrons to the two more electronegative chlorines to which it is bound, and neither gains nor loses electrons to the carbon (the β -carbon) to which it is doubly-bound. The oxidation state of the β -carbon is the same as that of the α -carbon, +II. Therefore, the average oxidation state of carbon is $(+II + II)/2 = +II$.



b. acetone

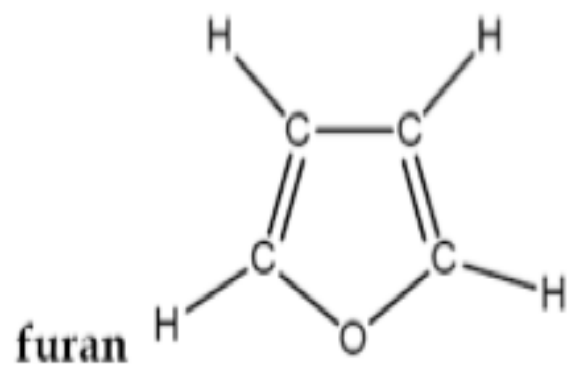
There are three carbons in acetone, two in methyl groups and one in the ketone group ($>\text{C}=\text{O}$). The oxidation state of the two carbons in the methyl groups is $-III$. They each gain three electrons from the less electronegative hydrogens. The oxidation state of the carbon in the ketone is $+II$. It loses two electrons to the more electronegative oxygen, one electron for each bond in the double bond. The average oxidation state of *carbon* is $(-III - III + II)/3 = -4/3$.

The oxidation state of the *oxygen* in acetone is $-II$. It gains two electrons from the less electronegative carbon through the double bond.



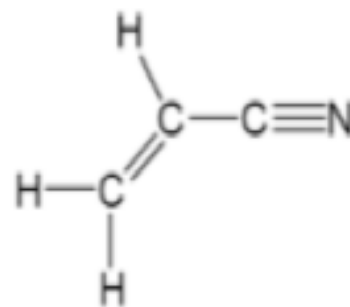
c. cyclohexene

Cyclohexene has carbons with two different oxidation states, the two carbons in the unsaturated double bond and four carbons in the saturated, aliphatic single bonds. The oxidation state of the two carbons in the double bond is -I. They each gain an electron from the less electronegative hydrogens to which they are bound. The oxidation state of the four carbons in the single bonds is -II. They each gain two electrons from the hydrogens to which they are bound. The average oxidation state of *carbon* is $(-I - I - II - II - II - II)/6 = -10/6 = -5/3$.

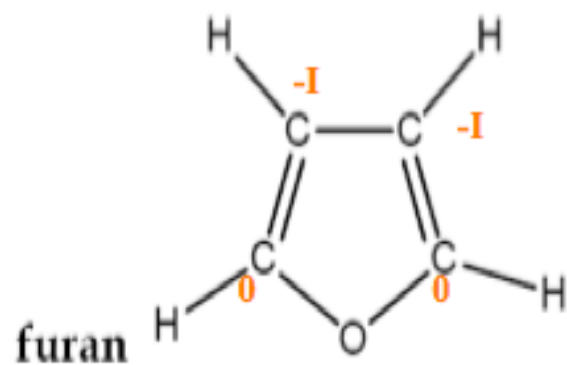


**Avg. oxidation state of
Carbon = $-1/2$**

acrylonitrile

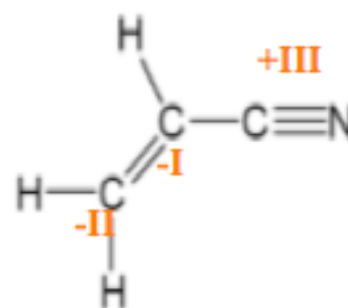


**Avg. oxidation state of
Carbon = 0**



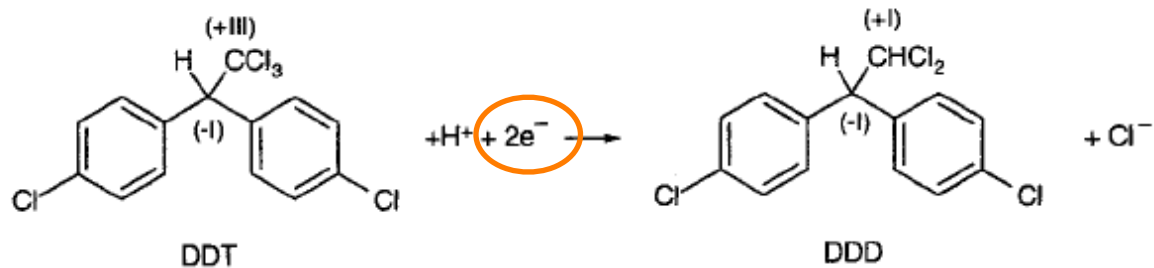
**Avg. oxidation state of
Carbon = $-1/2$**

acrylonitrile



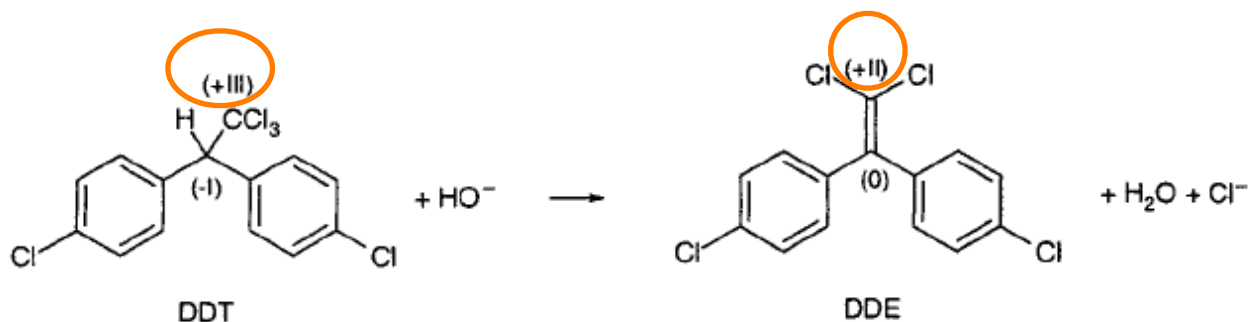
**Avg. oxidation state of
Carbon = 0**

Check the oxidation state of carbon, N, S



1,1'-(2,2,2-trichloroethylidene)bis[4-chlorobenzene]

1,1'-(2,2,2-dichloroethylidene)bis[4-chlorobenzene]



1,1'-(Dichloroethenylydene)bis[4-chlorobenzene]

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



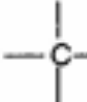
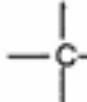
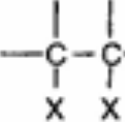
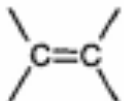
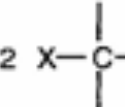
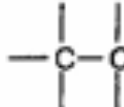
Oxidized Species	Reduction \rightleftharpoons Oxidation	Reduced Species	Equation Number
<i>Change in Oxidation State of Carbon Atom(s)</i>			
R-COOH + 2 H ⁺ + 2 e ⁻	←	R-CHO + H ₂ O	(14-4)
	\rightleftharpoons		(14-5)
	→		(14-6)
	→		(14-7)
	→		(14-8)

Table 13.2 Examples of Environmentally Relevant Chemical Reactions Involving Nucleophiles and/or Bases

Reactants		Products	Reaction Number
<i>Nucleophilic Substitutions at Saturated Carbon Atoms</i>			
$\text{CH}_3\text{Br} + \text{H}_2\text{O}$ Methyl bromide	→	$\text{CH}_3\text{OH} + \text{H}^+ + \text{Br}^-$ Methanol	(1)
$\text{CH}_3\text{Cl} + \text{HS}^-$ Methyl chloride	→	$\text{CH}_3\text{SH} + \text{Cl}^-$ Methane thiol (Methyl mercaptan)	(2)
$\text{CH}_3\text{O}-\overset{\text{O}}{\parallel}{\text{P}}(\text{OCH}_3)_2 + \text{H}_2\text{O}$ Trimethylphosphate	→	$\text{CH}_3\text{OH} + \text{}^-\text{O}-\overset{\text{O}}{\parallel}{\text{P}}(\text{OCH}_3)_2 + \text{H}^+$ Methanol Dimethylphosphate	(3)

13. Chemical Transformation I: Hydrolysis involving other Nucleophilic Species

Table 13.1 Examples of Important Environmental Nucleophiles

increasing nucleophilicity for reaction at a saturated carbon

ClO_4^-

H_2O

NO_3^-

F^-

$\text{SO}_4^{2-}, \text{CH}_3\text{COO}^-$

Cl^-

$\text{HCO}_3^-, \text{HPO}_3^{2-}$

NO_2^-

$\text{PhO}^{-a}, \text{Br}^-, \text{OH}^-$

I^-, CN^-

$\text{HS}^-, \text{R}_2\text{NH}^b$

$\text{S}_2\text{O}_3^{2-}, \text{SO}_3^{2-}, \text{PhS}^-$

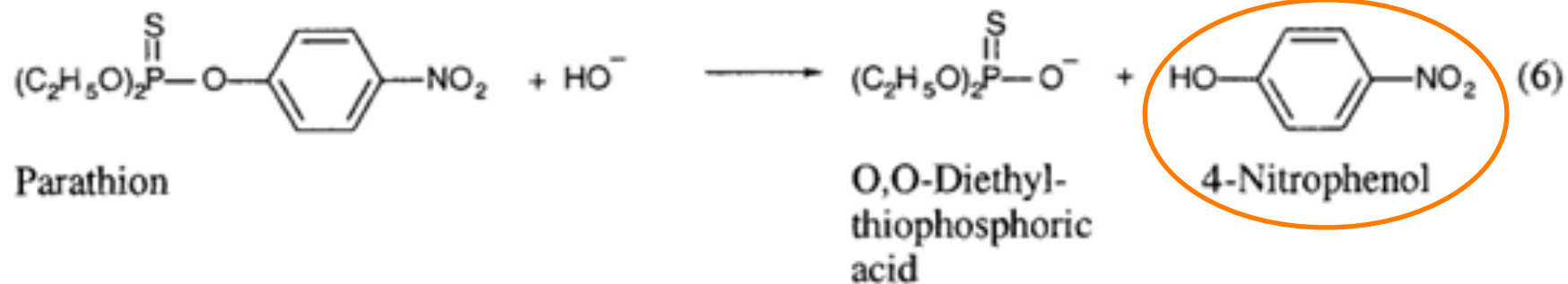
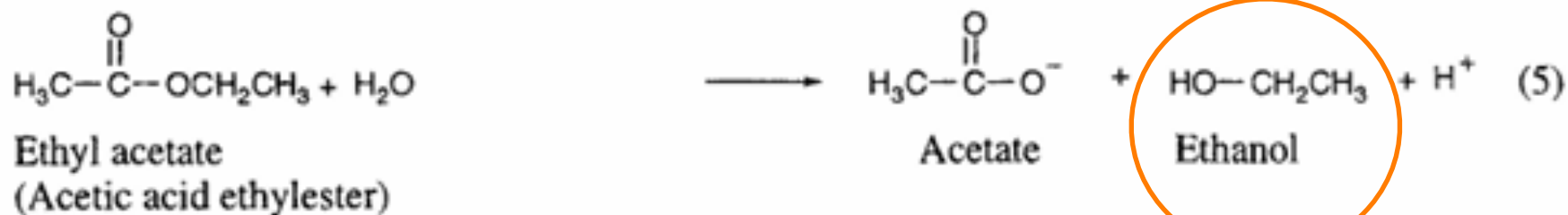
^a Ph = C₆H₅ (phenyl)

^b R = CH₃, C₂H₅

Table 13.2 Examples of Environmentally Relevant Chemical Reactions Involving Nucleophiles and/or Bases

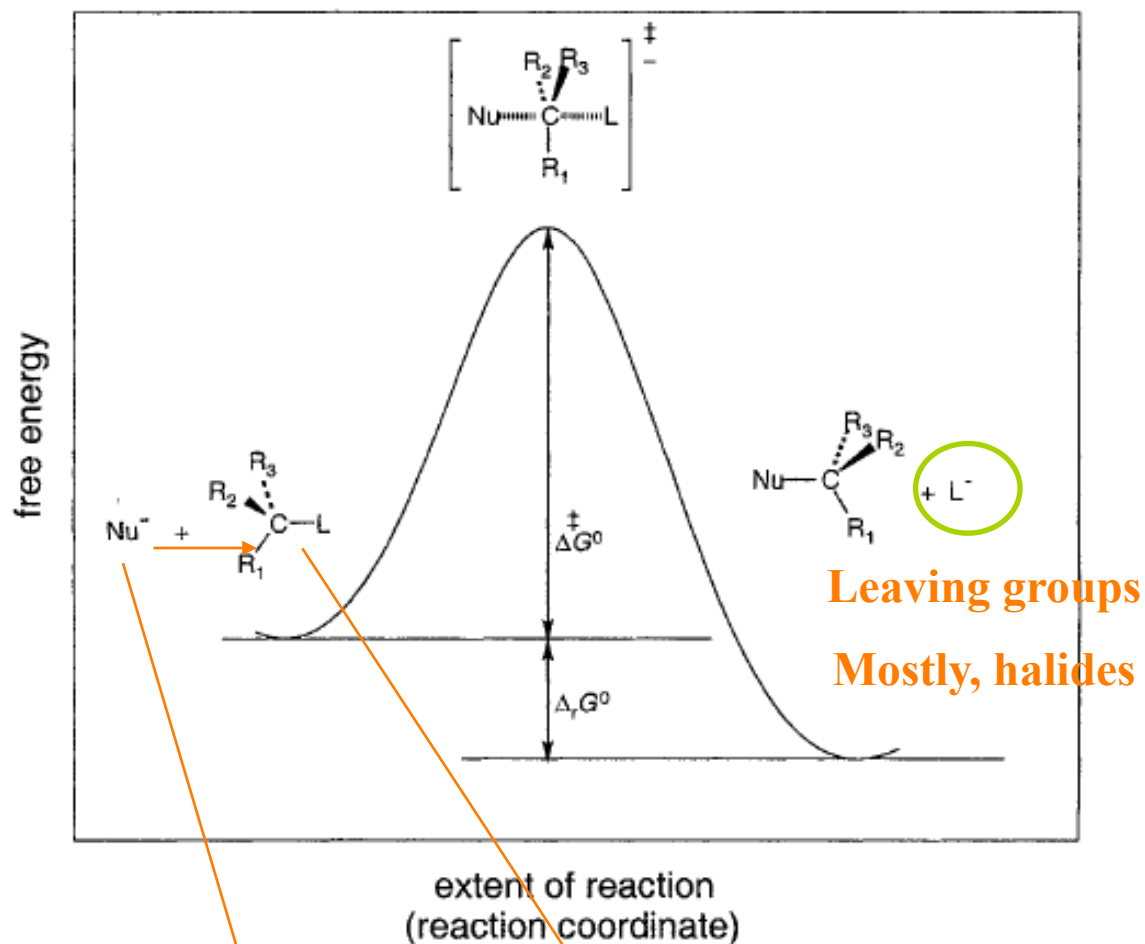
Reactants		Products	Reaction Number
<i>Nucleophilic Substitutions at Saturated Carbon Atoms</i>			
$\text{CH}_3\text{Br} + \text{H}_2\text{O}$ Methyl bromide	→	$\text{CH}_3\text{OH} + \text{H}^+ + \text{Br}^-$ Methanol	(1)
$\text{CH}_3\text{Cl} + \text{HS}^-$ Methyl chloride	→	$\text{CH}_3\text{SH} + \text{Cl}^-$ Methane thiol (Methyl mercaptan)	(2)
$\text{CH}_3\text{O}-\overset{\text{O}}{\parallel}{\text{P}}(\text{OCH}_3)_2 + \text{H}_2\text{O}$ Trimethylphosphate	→	$\text{CH}_3\text{OH} + \overset{\text{O}}{\parallel}{\text{O}}-\text{P}(\text{OCH}_3)_2 + \text{H}^+$ Methanol Dimethylphosphate	(3)

Ester Hydrolysis



Rxn. (6) is more favored, why?

Figure 13.1 Two-dimensional portrayal of relative free energies exhibited by the reactants, activated complex, and products of an S_N2 reaction.



Substitution, nucleophilic, bimolecular

thus, S_N2

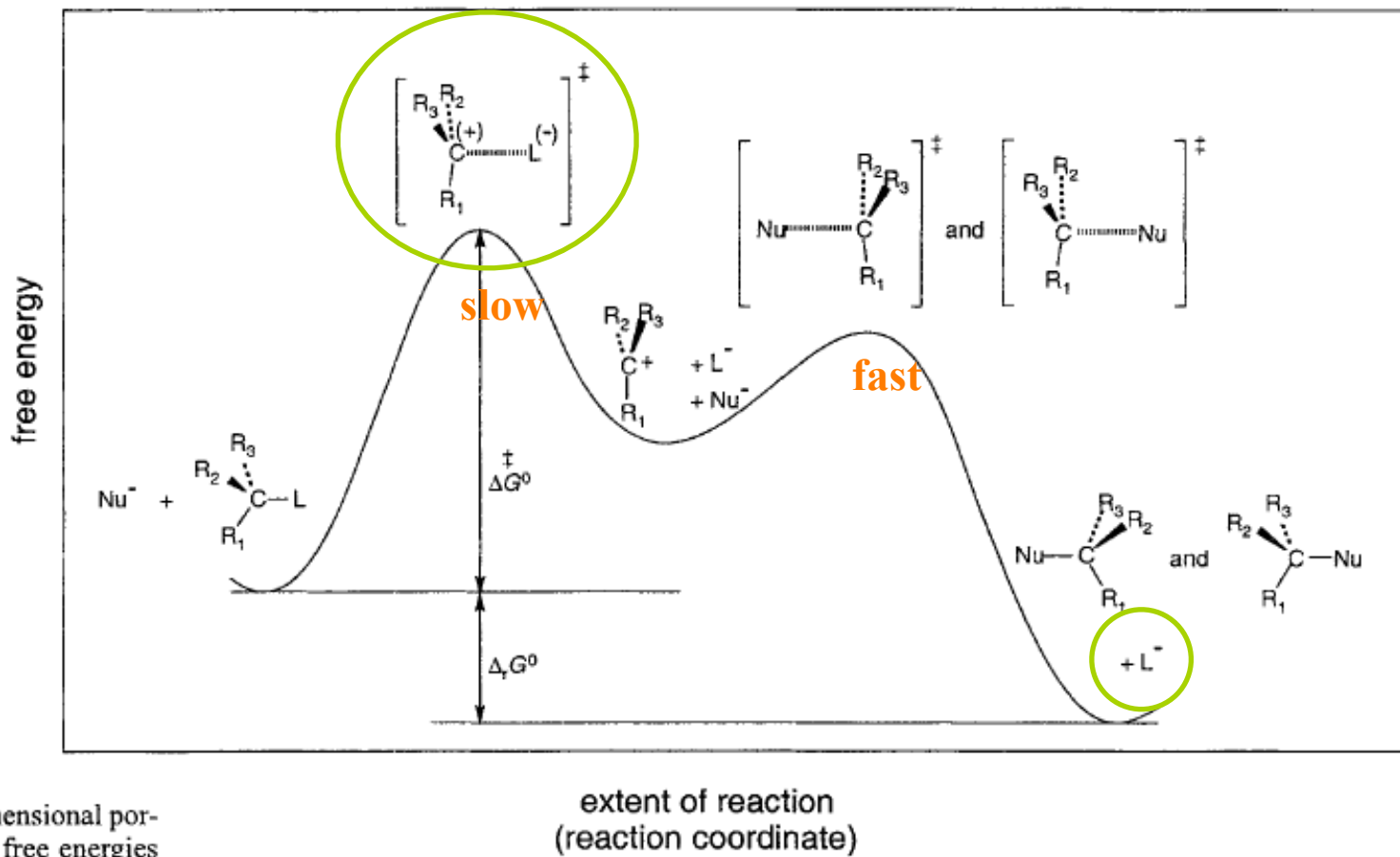


Figure 13.2 Two-dimensional portrayal of the relative free energies exhibited by reactants, activated complex, an intermediate, and product of an S_N1 reaction.

rates various electronic and steric factors that are strongly determined by the struc-

Substitution, nucleophilic, unimolecular

thus, S_{N1}

Table 13.1 Examples of Important Environmental Nucleophiles

increasing nucleophilicity for reaction at a saturated carbon

ClO_4^-

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NO_3^-

F^-

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Cl^-

$\text{HCO}_3^-, \text{HPO}_3^{2-}$

NO_2^-

$\text{PhO}^{-a}, \text{Br}^-, \text{OH}^-$

I^-, CN^-

$\text{HS}^-, \text{R}_2\text{NH}^b$


$\text{S}_2\text{O}_3^{2-}, \text{SO}_3^{2-}, \text{PhS}^-$

^a Ph = C₆H₅ (phenyl)

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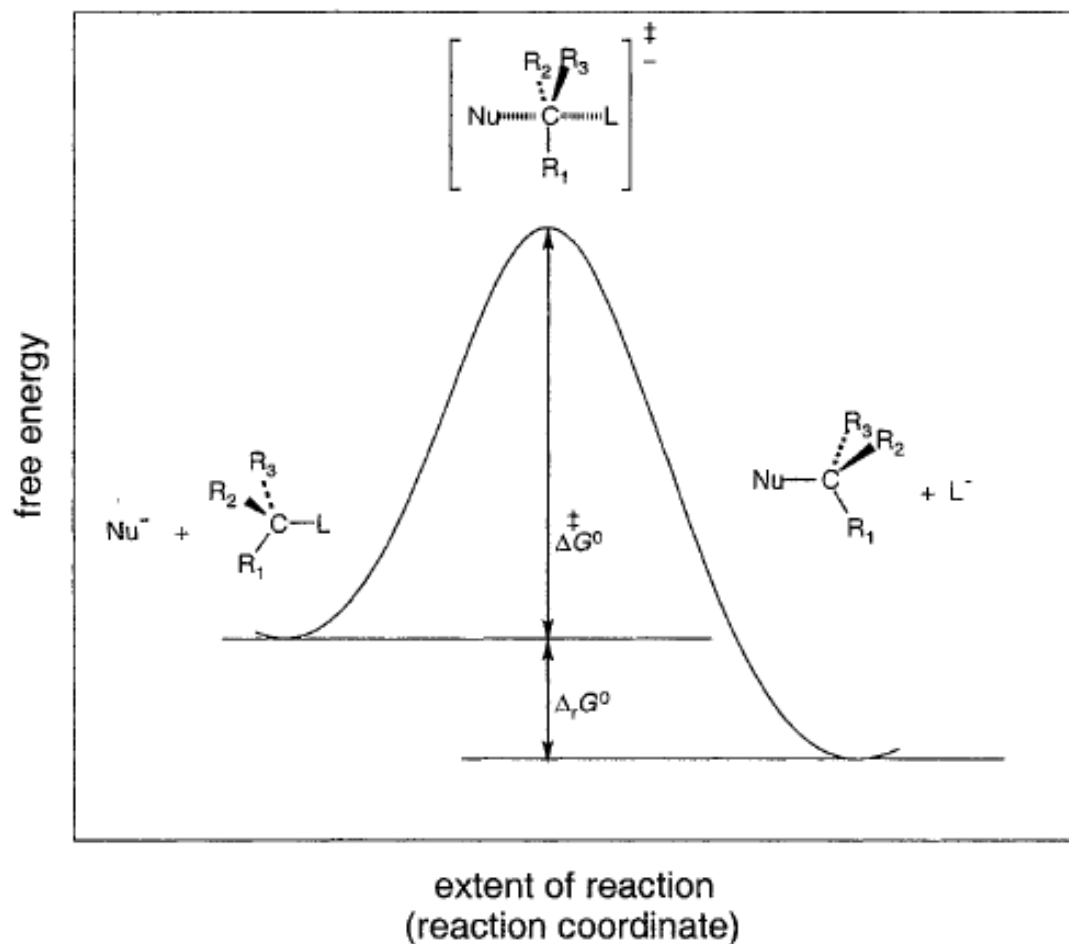


ClO_4^-
H_2O
NO_3^-
F^-
$\text{SO}_4^{2-}, \text{CH}_3\text{COO}^-$
Cl^-
$\text{HCO}_3^-, \text{HPO}_3^{2-}$
NO_2^-
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I^-, CN^-
$\text{HS}^-, \text{R}_2\text{NH}^b$
$\text{S}_2\text{O}_3^{2-}, \text{SO}_3^{2-}, \text{PhS}^-$

^a Ph = C₆H₅ (phenyl)

^b R = CH₃, C₂H₅

Figure 13.1 Two-dimensional portrayal of relative free energies exhibited by the reactants, activated complex, and products of an S_N2 reaction.



S_N2

$$\frac{d[\text{R}_1\text{R}_2\text{R}_3\text{C-L}]}{dt} = -k[\text{Nu}^-][\text{R}_1\text{R}_2\text{R}_3\text{C-L}] \quad (13-1)$$

where k is a second-order rate constant (e.g., $\text{M}^{-1} \text{s}^{-1}$).

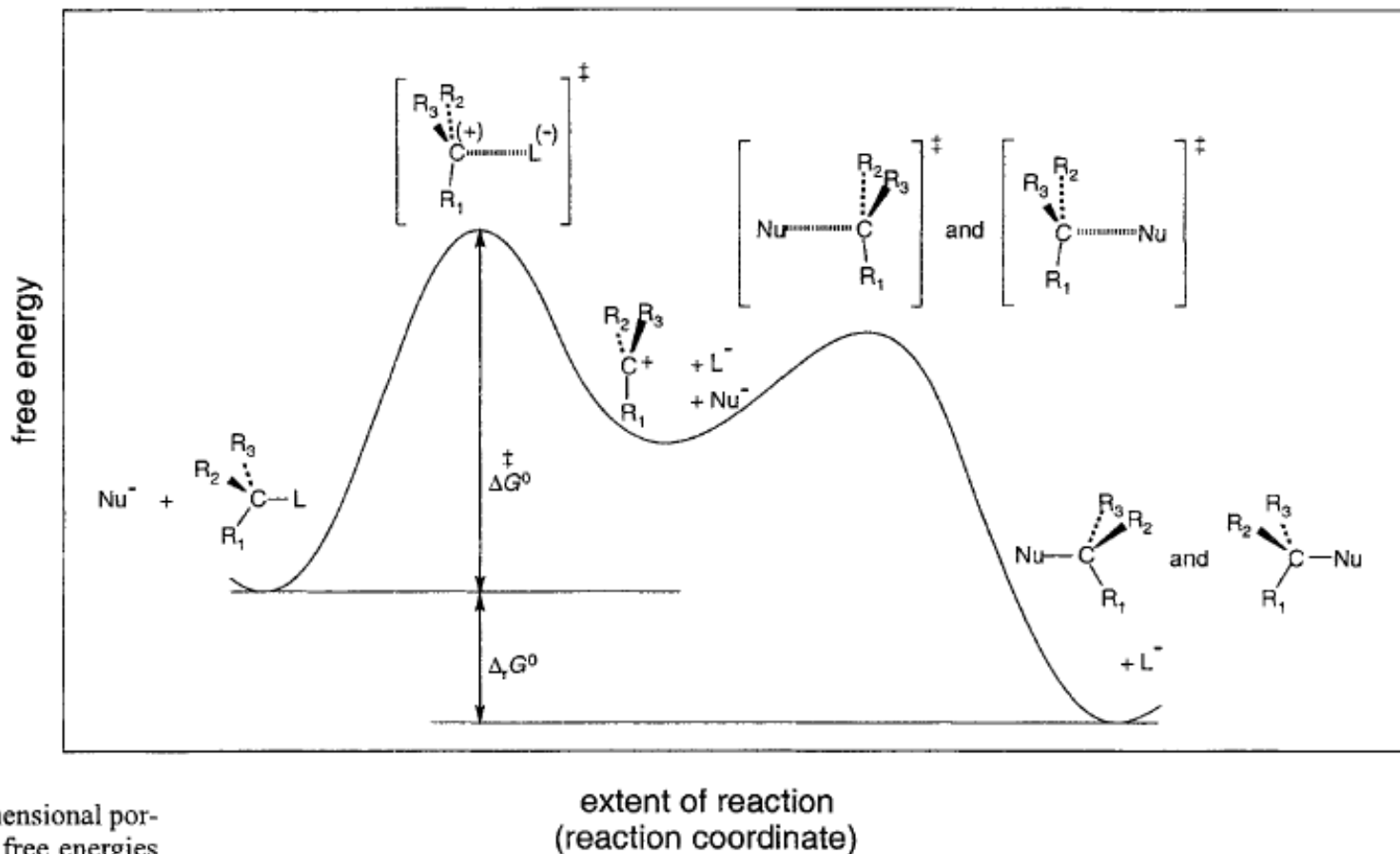


Figure 13.2 Two-dimensional portrayal of the relative free energies exhibited by reactants, activated complex, an intermediate, and product of an S_N1 reaction.

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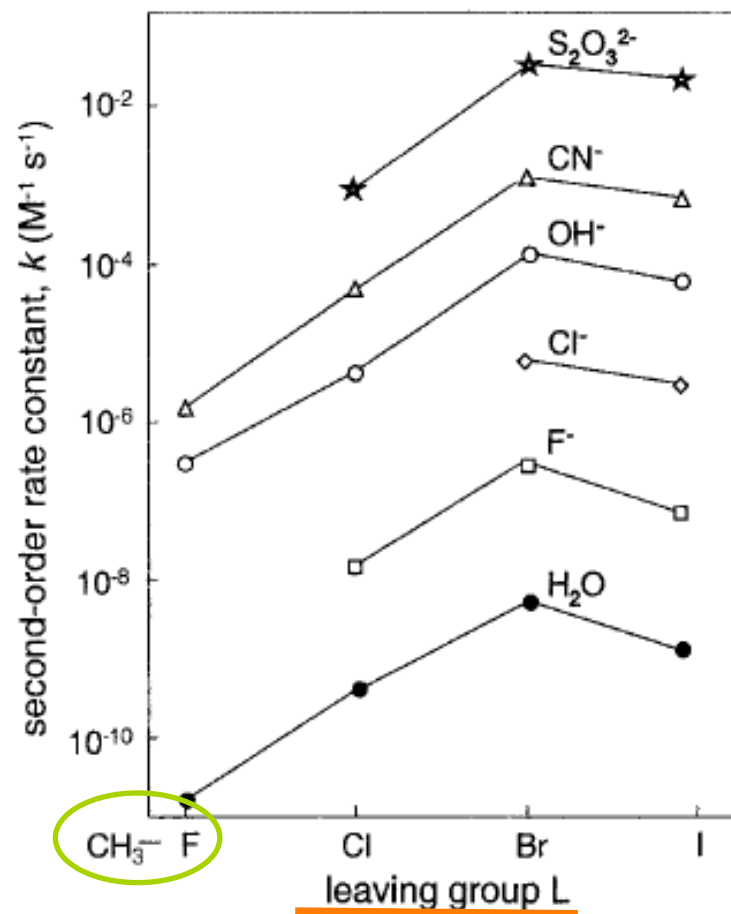
S_N1

$$\frac{d[R_1R_2R_3C-L]}{dt} = -k[R_1R_2R_3C-L] \quad (13-2)$$

where k is now a first-order rate constant (e.g., s^{-1}). The reaction is then said to occur

We understand "k" for S_N rxns;
next, how can we determine the "k"?

Figure 13.3 Rate constants for reactions of methyl halides with various nucleophiles (data from Hughes, 1971; Mabey and Mill, 1978).



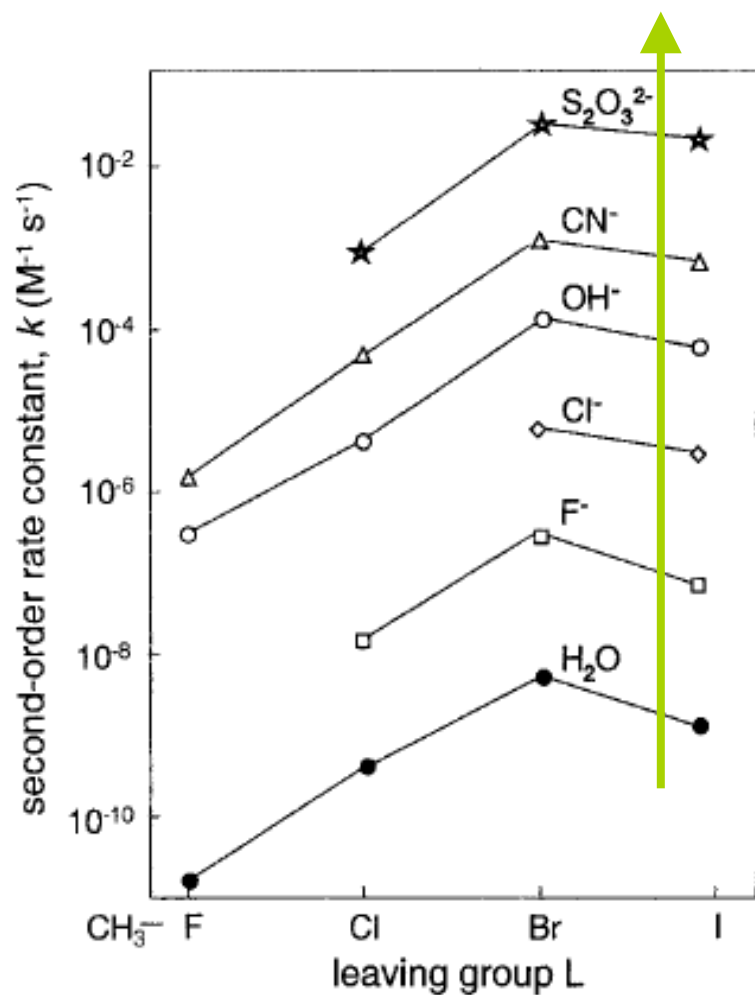


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	<u>H_2O</u>
	NO_3^-
	<u>F^-</u>
	$\text{SO}_4^{2-}, \text{CH}_3\text{COO}^-$
	<u>Cl^-</u>
	$\text{HCO}_3^-, \text{HPO}_3^{2-}$
	NO_2^-
	$\text{PhO}^{-a}, \text{Br}^-, \text{OH}^-$
	<u>I^-, CN^-</u>
$\text{HS}^-, \text{R}_2\text{NH}^b$	
<u>$\text{S}_2\text{O}_3^{2-}, \text{SO}_3^{2-}, \text{PhS}^-$</u>	

^a Ph = C_6H_5 (phenyl)

^b R = $\text{CH}_3, \text{C}_2\text{H}_5$

$$\log\left(\frac{k_{\text{Nu}}}{k_{\text{H}_2\text{O}}}\right) = s \cdot n_{\text{Nu,CH}_3\text{Br}} \quad (13-3)$$

here k_{Nu} is the *second-order* rate constant for a nucleophilic displacement by a nucleophile of interest, $k_{\text{H}_2\text{O}}$ is the *second-order* rate constant for nucleophilic attack by water (the standard nucleophile), n is a measure of the attacking aptitude or nucleophilicity of the nucleophile of interest, and s reflects the sensitivity of the organic molecule to nucleophilic attack. The n values of some important environmental nucleophiles determined for the reaction with *methyl bromide* (CH_3Br) in aqueous solution are given in Table 13.3. It should be pointed out that currently, particularly in pharmaceutical, toxicological, and basic chemical applications (Hansch and Leo, 1995), the relative nucleophilicity of inorganic and organic nucleophiles is quantified using another reference reaction, substitution of *methyl iodide* (CH_3I) in *methanol*:

$$\log\left(\frac{k_{\text{Nu}}}{k_{\text{CH}_3\text{OH}}}\right) = s' \cdot n_{\text{Nu,CH}_3\text{I}} \quad (13-4)$$

Table 13.3 Relative Nucleophilicities of Some Important Environmental Nucleophiles: n -Values Determined from the Reaction with Methyl Bromide or n -Hexyl Bromide in Water (Eq. 13-3, $s = 1$)

Nucleophile	$n_{\text{Nu,CH}_3\text{Br}}^a$
ClO_4^-	<0
H_2O	0
NO_3^-	1.0
F^-	2.0
SO_4^{2-}	2.5
CH_3COO^-	2.7
Cl^-	3.0
HCO_3^- , HPO_4^{2-}	3.8
Br^-	3.9
OH^-	4.2
I^-	5.0
CN^- , HS^-	5.1
$\text{S}_2\text{O}_3^{2-}$	6.1 ^b
PhS^-	6.8 ^b
S_4^{2-}	7.2 ^b

^a Data from Hine (1962). ^b Data from Haag and Mill (1988a).

Table 13.4 Relative Nucleophilicities of Some Important Environmental Nucleophiles: n -Values Determined From the Reaction with Methyl Iodide in Methanol (Eq. 13-4, $s' = 1$)

Nucleophile	$n_{\text{Nu,CH}_3\text{I}}^a$
CH_3OH	0
NO_3^-	~1.5
F^-	~2.7
SO_4^{2-}	3.5
HCO_3^{2-} , HPO_4^{2-}	3.8
CH_3COO^-	4.4
Cl^-	4.4
Pyridine	5.2
PhNH_2	5.7
PhO^-	5.8
Br^- , N_3^-	5.8
CN^-	6.7
$(\text{C}_2\text{H}_5)_2\text{NH}$	~7.0
I^-	7.4
HS^-	~8
$\text{S}_2\text{O}_3^{2-}$	8.9
PhS^-	9.9

^a Data from Pearson et al. (1968).

**Relative Importance with regard to
*“Water”***

Table 13.5 Calculated
Concentration of Nucleophile
Required to Compete with Water
 in an S_N2 Reaction with Alkyl
 Halides Assuming an s Value of 1

Nucleophile	$[\text{Nu}]_{50\%}^a$ (M)
NO_3^-	~ 6
F^-	$\sim 6 \times 10^{-1}$
SO_4^{2-}	$\sim 2 \times 10^{-1}$
Cl^-	$\sim 6 \times 10^{-2}$
HCO_3^-	$\sim 9 \times 10^{-3}$
HPO_4^-	$\sim 9 \times 10^{-3}$
Br^-	$\sim 7 \times 10^{-3}$
OH^-	$\sim 4 \times 10^{-3}$
I^-	$\sim 6 \times 10^{-4}$
HS^-	$\sim 4 \times 10^{-4}$
CN^-	$\sim 4 \times 10^{-4}$
$\text{S}_2\text{O}_3^{2-}$	$\sim 4 \times 10^{-5}$
S_4^{2-}	$\sim 4 \times 10^{-6}$

^a Eq. 13-5 using the $n_{\text{Nu},\text{CH}_3\text{Br}}$ values given in Table 13.3.

But, in seawater



Illustrative Example 13.2 Some More Reactions Involving Methyl Bromide

Problem

Estimate the half-life in days (with respect to chemical transformation) of methyl bromide (CH_3Br) present at low concentration (i.e., $< 1 \text{ mM}$) in a homogeneous aqueous solution ($\text{pH} = 7.0$, $T = 25^\circ\text{C}$) containing 100 mM Cl^- , 2 mM NO_3^- , 1 mM HCO_3^- , and 0.1 mM CN^- . In pure water at $\text{pH} 7.0$ and 25°C , the half-life of CH_3Br is about 20 days.

$$k_{\text{obs}} = k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + \sum_j k_{\text{Nu}_j}[\text{Nu}_j]$$

Table 13.5 Calculated Concentration of Nucleophile Required to Compete with Water in an $\text{S}_{\text{N}}2$ Reaction with Alkyl Halides Assuming an s Value of 1

Nucleophile	$[\text{Nu}]_{50\%}^a$ (M)
NO_3^-	~ 6
F^-	$\sim 6 \times 10^{-1}$
SO_4^{2-}	$\sim 2 \times 10^{-1}$
Cl^-	$\sim 6 \times 10^{-2}$
HCO_3^-	$\sim 9 \times 10^{-3}$
HPO_4^-	$\sim 9 \times 10^{-3}$
Br^-	$\sim 7 \times 10^{-3}$
OH^-	$\sim 4 \times 10^{-3}$
I^-	$\sim 6 \times 10^{-4}$
HS^-	$\sim 4 \times 10^{-4}$
CN^-	$\sim 4 \times 10^{-4}$
$\text{S}_2\text{O}_3^{2-}$	$\sim 4 \times 10^{-5}$
S_4^{2-}	$\sim 4 \times 10^{-6}$

We can neglect NO_3^- , OH^- ; why?

$\text{pH} = 7.0$, thus, concentration of OH^-

^a Eq. 13-5 using the $n_{\text{Nu,CH}_3\text{Br}}$ values given in Table 13.3.

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$$k_{\text{Nu}} = k_{\text{H}_2\text{O}} \cdot 10^{n_{\text{Nu,CH}_3\text{Br}}} \quad (2)$$

$n_{\text{Nu,CH}_3\text{Br}}$ values from Table 13.3 into Eq. 2, and substitute k_{Nu} for each nucleophile into Eq. 1:

$$k_{\text{obs}} = k_{\text{H}_2\text{O}} \{ [\text{H}_2\text{O}] + 10^3 [\text{Cl}^-] + 10^{3.8} [\text{HCO}_3^-] + 10^{5.1} [\text{CN}^-] \} \quad (3)$$

Now, the only unknown is $K_{\text{H}_2\text{O}}$

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Problem

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$$t_{1/2} = \frac{\ln 2}{k_N} = \frac{\ln 2}{k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]}$$

Use the reported hydrolysis half-life (20d) to find:

$$k_{\text{H}_2\text{O}} = \frac{0.693}{(55.3 \text{ M})(20\text{d})} = 6.3 \times 10^{-4} \text{ M}^{-1} \text{ d}^{-1}$$

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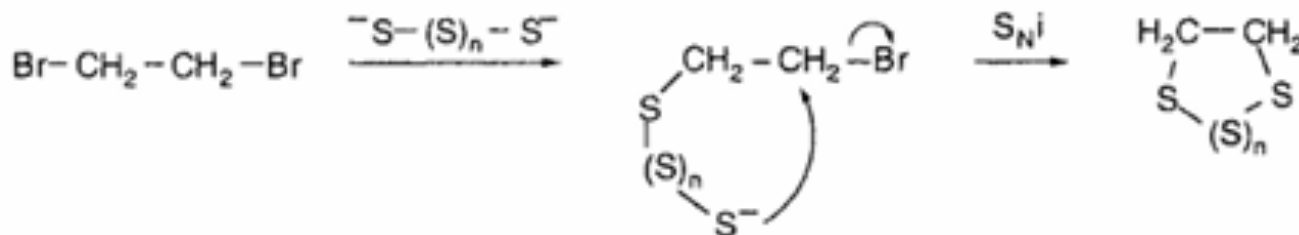
$n_{\text{Nu,CH}_3\text{Br}}$ values from Table 13.3 into Eq. 2, and substitute k_{Nu} for each nucleophile into Eq. 1:

$$k_{\text{obs}} = k_{\text{H}_2\text{O}} \{ [\text{H}_2\text{O}] + 10^3 [\text{Cl}^-] + 10^{3.8} [\text{HCO}_3^-] + 10^{5.1} [\text{CN}^-] \} \quad (3)$$

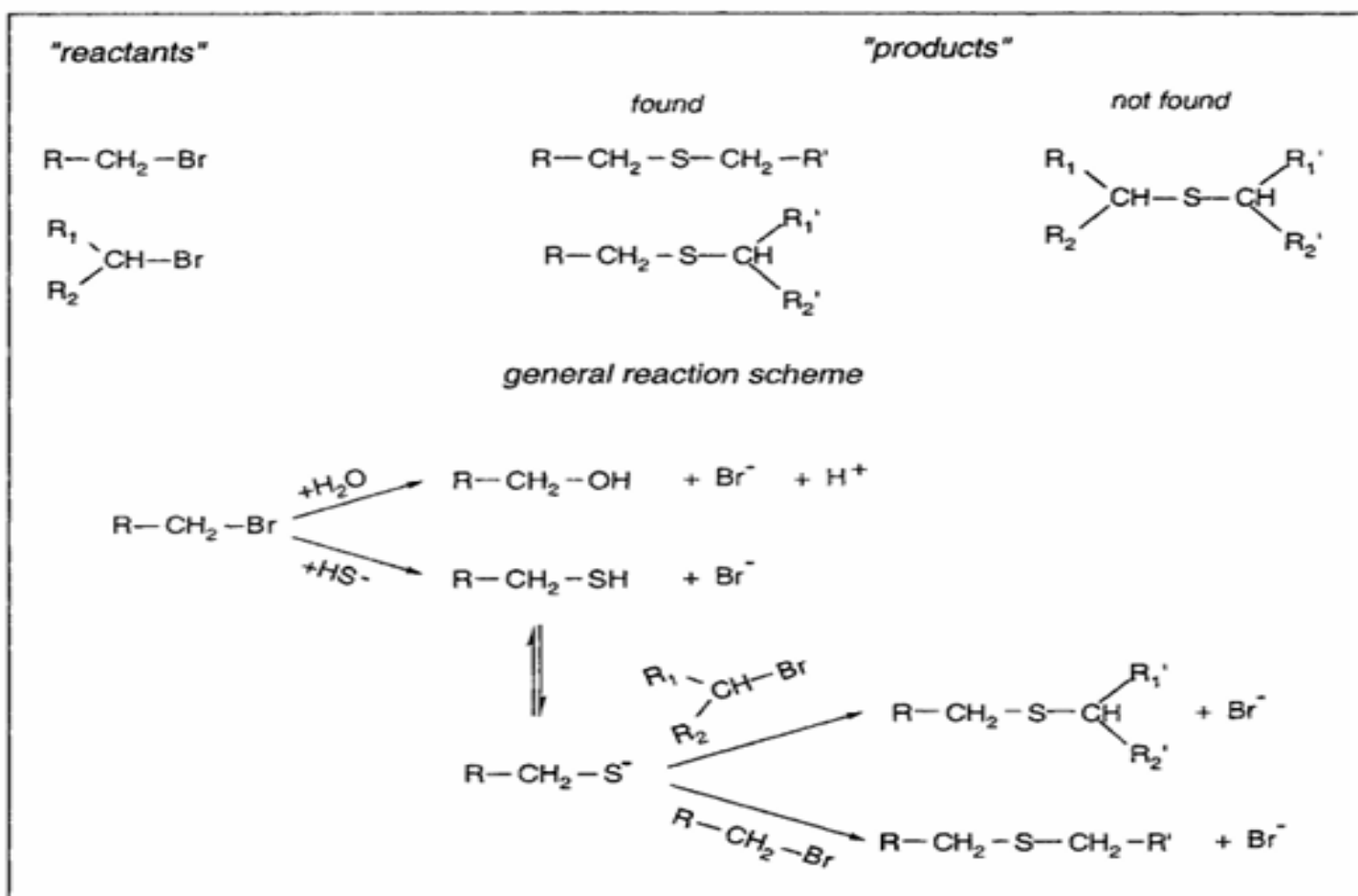
$$k_{\text{obs}} = k_{\text{H}_2\text{O}} (55.5 + 100 + 6.3 + 12.6) = k_{\text{H}_2\text{O}} (174.4)$$

$$t_{1/2} = \frac{\ln 2}{k_{\text{obs}}} = \frac{0.693}{(6.3 \times 10^{-4} \text{ M}^{-1} \text{ d}^{-1})(174.4 \text{ M})} = \sim 6 \text{ d}$$

Examples under sulfate reducing conditions

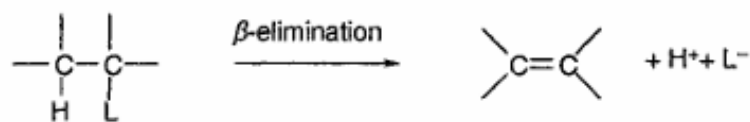


$\text{S}_\text{N}1$



Polyhalogenated Alkanes-Elimination Mechanisms

Table 13.7: $t_{1/2}$ so long, thus, very slow rxns.



dehydrohalogenation

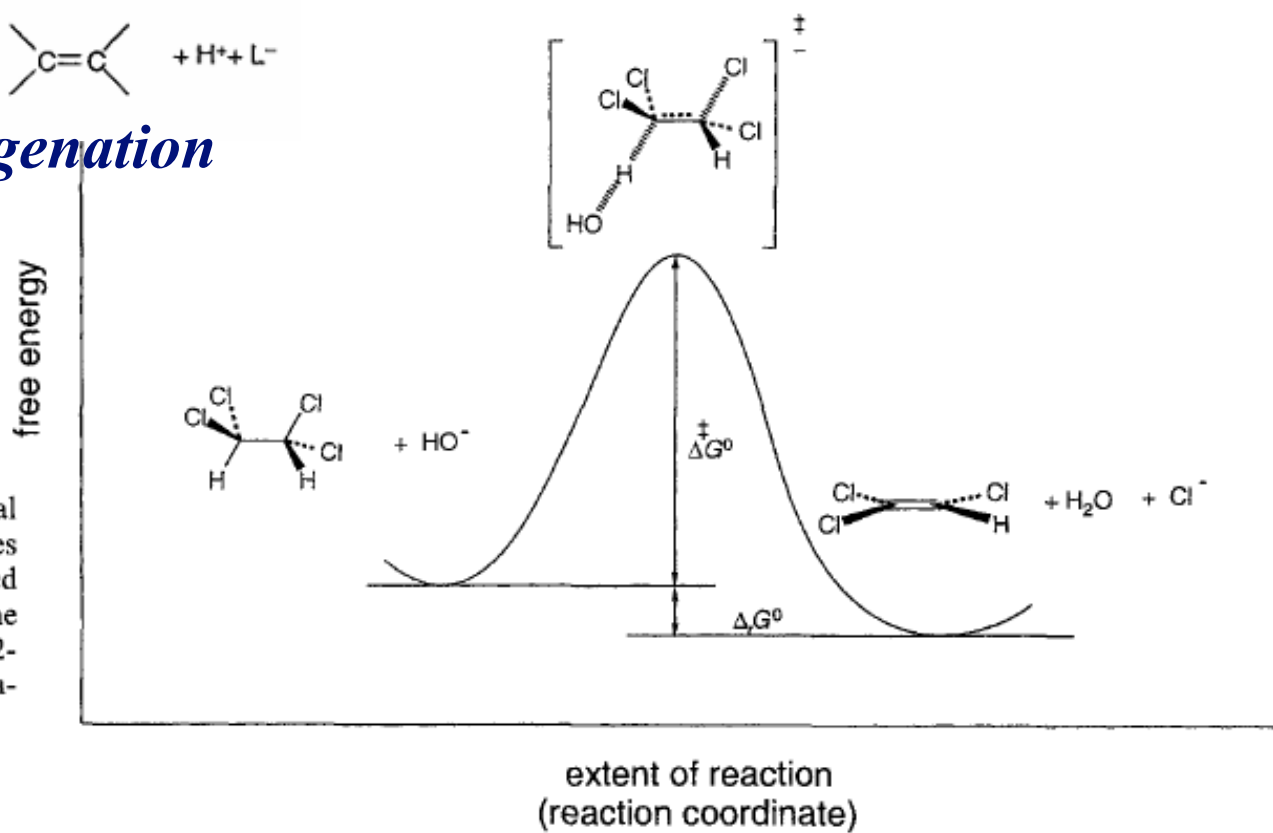
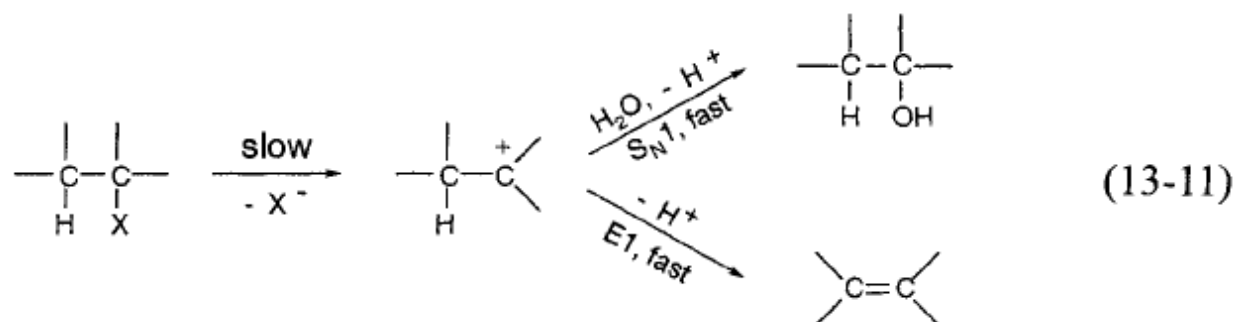


Figure 13.6 Two-dimensional portrayal of relative free energies exhibited by the reactants, activated complex, and products of the β -elimination reactions of 1,1,2,2-tetrachloroethane by an E2 mechanism.

Elimination, adjacent, two removed

thus, E₂; β -elimination



$$\text{rate} = - \left\{ k_{\text{N}} + k_{\text{EN}} + (k_{\text{B}} + k_{\text{EB}})[\text{OH}^-] + \sum_j k_{\text{Nu}_j} [\text{Nu}_j] \right\} C_{iw} \quad (13-12)$$

where C_{iw} is the concentration of the dissolved halogenated compound i in water, k_{N} and k_{EN} are the (pseudo)first-order rate constant for the neutral, and k_{B} and k_{EB} are the second-order rate constants for the base-catalyzed hydrolysis and elimination reactions, respectively, and k_{Nu_j} is the second-order rate constant of the $\text{S}_{\text{N}}2$ reaction with other particular nucleophile j . Note that k_{Nu_j} may be estimated using the Swain-Lupton relationship (Eq. 13-6). We recall that by assuming constant pH and constant nucleophile concentration(s), Eq. 13-12 can be reduced to a pseudo-first-order rate with a pseudo-first-order rate constant k_{obs} that is given by:

$$k_{\text{obs}} = k_{\text{N}} + k_{\text{EN}} + (k_{\text{B}} + k_{\text{EB}})[\text{OH}^-] + \sum_j k_{\text{Nu}_j} [\text{Nu}_j] \quad (13-13)$$