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CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #14

Prediction Methods: Going beyond Hammett II

Brezonik, pp.553-578

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Introduction

Oxidation I

- 3D QSAR models

Table 12.10
Descriptors and properties generated by QikProp used for QSPR model development

Descriptor/Property	Explanation
Molecular descriptor	
MW, volume	Molecular weight and volume
SASA, FOSA, FISA, PISA, WPSA	Molecular surface area, hydrophobic, hydrophilic, π and weakly polar component of surface area
#amine, #amidine, #acid, #amide	Number of non-conjugated functional groups for each type
#rotor	Number of non-trivial (not CX_3), non-hindered (not alkene, amide, small ring) rotatable bonds
#rctvFG, #metabol	Number of reactive functional groups, number of metabolites
donorHB, accptHB	Number of hydrogen bonding donated or accepted by the solute from water
dipole	Dipole moment
QPpolrz	Polarizability
IP, EA	Ionization potential and electron affinity
Physicochemical properties	
S	Solubility
QplogPC16	Hexadecane/gas partition coefficient
QPlogPoct	Octanol/gas partition coefficient
QPlogPw	Water/gas partition coefficient
QplogPo/w	Octanol/water partition coefficient

Snyder et al., 2007 ***"Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes"*** **[AWWARF final report]**

Oxidation II

- results

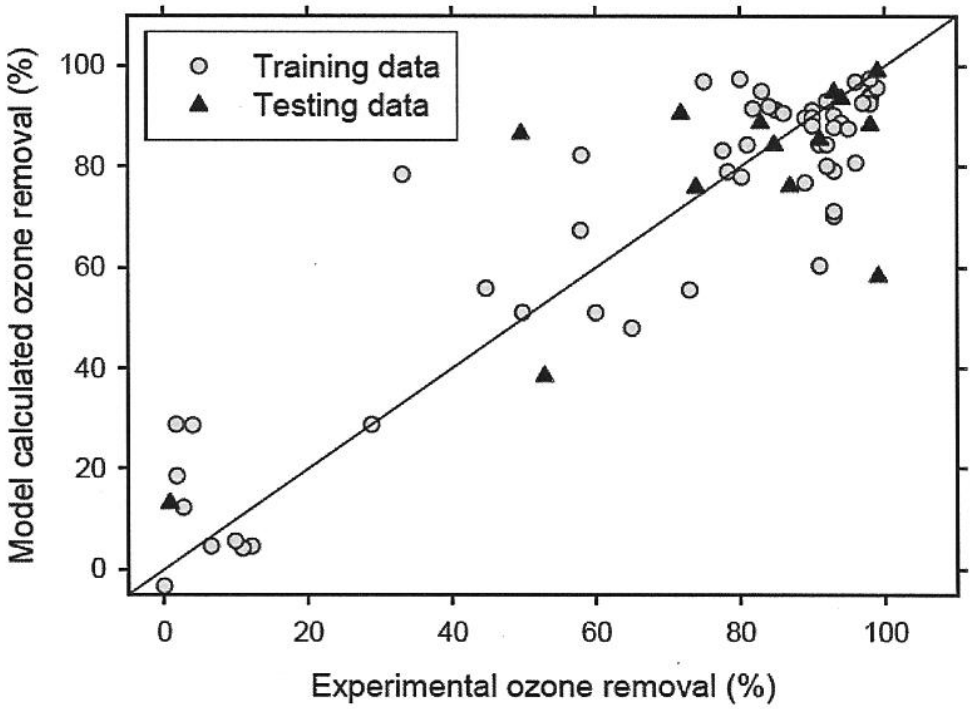


Figure 12.4 Comparison between the experimental obtained ozone removal of selected EDCs and PPCPs and model calculated results

Snyder et al., 2007 ***"Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes"*** **[AWWARF final report]**

UF I

- Stepwise addition

Table 12.11
Evolvement of significant dependent variables in QSPR modeling for the UF membrane

# of descriptors	#acid	H bond	QPpolrz	#amide	IP	QPlogS	Log Kow	R^2
6	√	√	√	√	√	√	×	0.645
5	√	√	√	√	√	×	×	0.643
4	√	√	√	√	×	×	×	0.638
3	√	√	√	×	×	×	×	0.615
2	√	×	×	×	×	×	√	0.562
1	×	×	×	×	×	×	√	0.396

T value decreasing

Note: √ indicates a parameter found significant in the model and x indicates a parameter excluded from the model

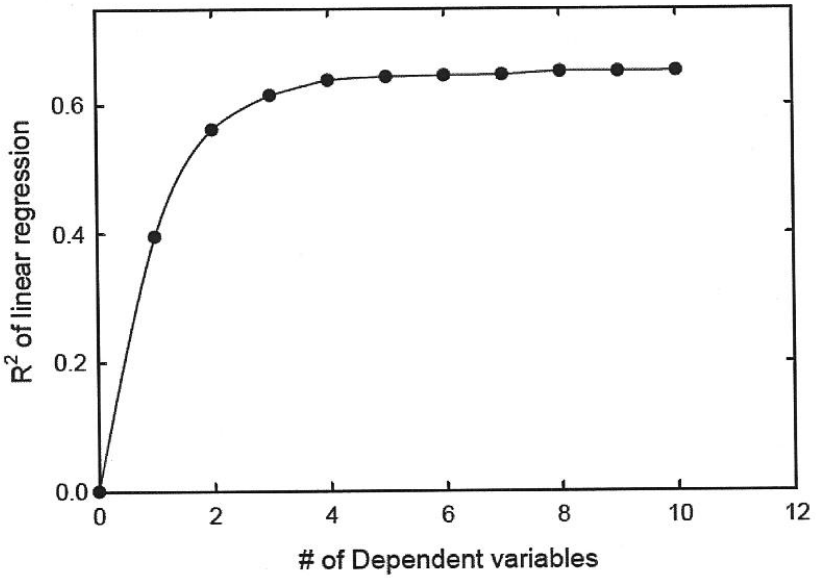


Figure 12.5 Progress in R^2 as the number of dependent variables increases

Snyder et al., 2007 *"Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes"* [AWWARF final report]

UF II

- results

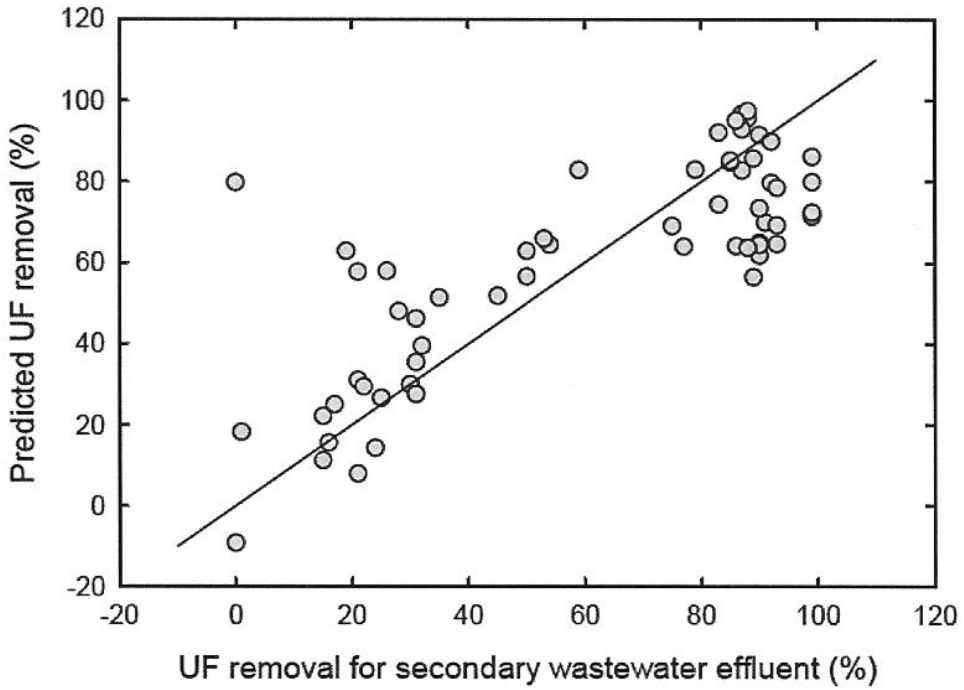


Figure 12.6 Comparison between the experimental obtained UF removal of selected EDCs and PPCPs and model calculated results

Acid/Base

- Summary reactions
  - Pg.171 in Brezonik

Table 4-1. Mechanisms of Acid-Base Catalysis

Type	Mechanism	Rate expression	Comments
I. Specific H^+	$S + HA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$ $SH^+ + H_2O \xrightarrow[\text{slow}]{k_3} P + H_3O^+$	$P = k_1k_3[S][HA]/k_2[A^-]$ $= (k_1k_3/k_2K_a)[S][H^+]$ where $K_a = [H^+][A^-]/[HA]$	For protolytic case, expression applies when $k_3 \ll k_2[A^-]$ whether initial H^+ transfer is from Bronsted acid (HA) or H_3O^+.
II. General acid	$S + HA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$ $SH^+ + H_2O \xrightarrow[\text{fast}]{k_3} P + H_3O^+$	$P = [S]\{\Sigma k_i[HA]\}$	Expression applies when $k_3 \gg k_2[A^-]$; rate-controlling step is formation of intermediate SH^+. P written for presence of several Bronsted acids in system.
III. General acid	$S + HA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$ $SH^+ + A^- \xrightarrow{k_3} P + HA$	$P = \frac{k_1k_3[S][HA]}{(k_2 + k_3)}$ or $P = k'[S][HA]$	Prototropic mechanism yields general acid catalysis regardless of relative sizes of k_2 and k_3.
IV. Specific OH^-	$HS + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S^- + BH^+$ $S^- + H_2O \xrightarrow[\text{slow}]{k_3} P + OH^-$	$P = k_1k_3[S^-][B]/k_2[BH^+]$ $= (k_1k_3/k_2K_B)[S^-][OH^-]$	For protolytic case, expression applies when $k_3 \ll k_2[BH^+]$ regardless of nature of proton acceptor in first step.
V. General base	$HS + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S^- + BH^+$ $S^- + H_2O \xrightarrow[\text{fast}]{k_3} P + OH^-$	$P = k[HS][B]$ $P = [HS]\{\Sigma k_i[B_i]\}$	Expression applies when $k_3 \gg k_2[BH^+]$; rate-controlling step is formation of S^-; P written for presence of several Bronsted bases.
VI. General base	$HS + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S^- + BH^+$ $S^- + BH^+ \xrightarrow{k_3} P + B$	$P = \frac{k_1k_3[S][HA]}{(k_2 + k_3)}$ or $P = k'[S][HA]$	Prototropic case yields general base catalysis regardless of relative sizes of k_2 and k_3.

Adapted from Laidler, K. J., *Chemical Kinetics*, McGraw-Hill, New York, 1965.

- Mechanisms 1
  - Pg. 172

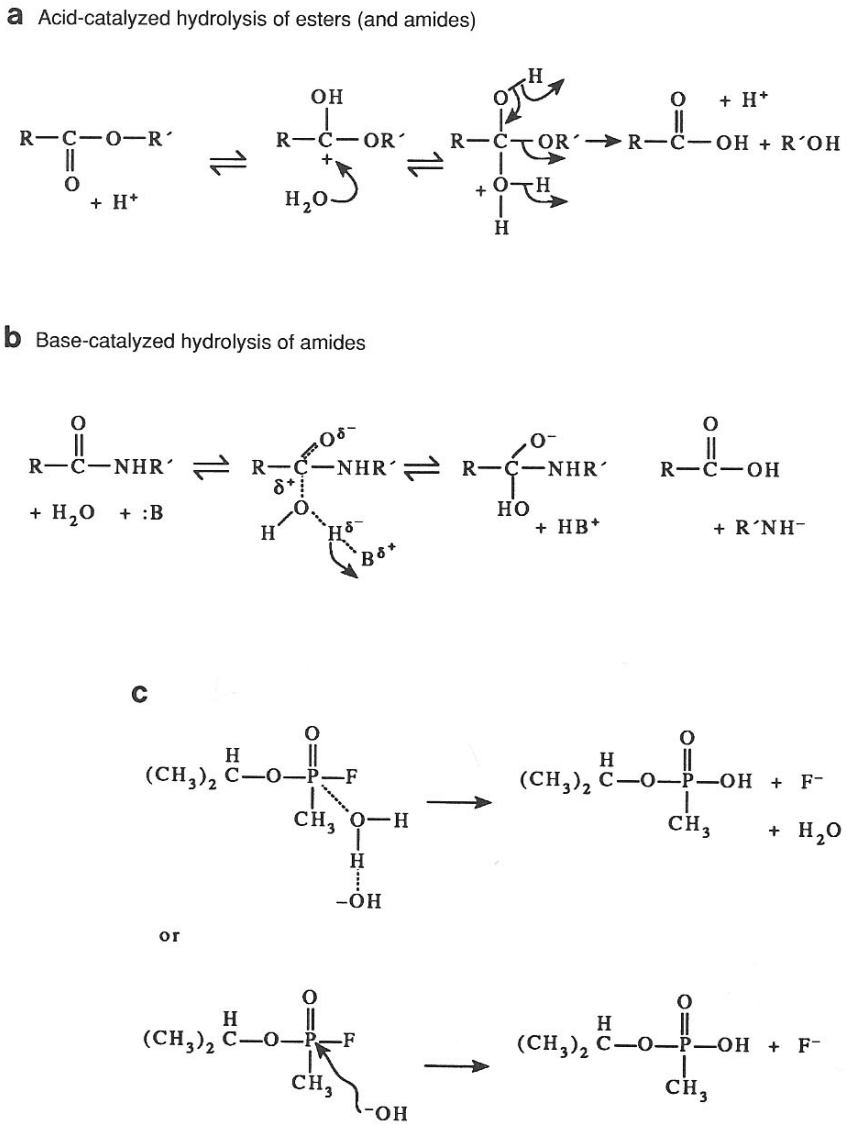
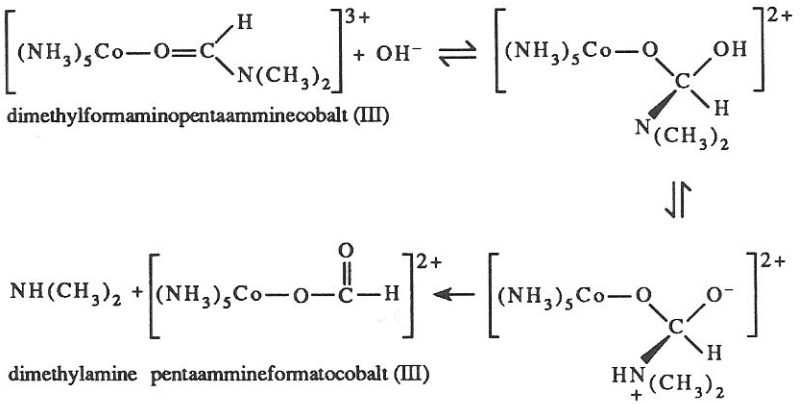


Figure 4-1. Mechanisms of acid-, base-, and metal-catalyzed reactions of various compounds and classes of compounds: (a) H^+, esters; (b) Bronsted base, amides; (c) OH^-, sarin (a neurotoxin); (d) OH^-, octahedral metal-amine complexes; (e) heavy metals, amides, peptides; (f) intramolecular Co^{III}-assisted, glycylglycine; (g) intramolecular M^{II}-assisted, imidazole methyl esters; (h) pH-independent, metal-catalyzed, 2-pyridylmethyl hydrogen phthalate ester; (i) Cu^{II}, parathion; (j) transition metals, oxaloacetate decarboxylation; (k) M^{II}, adenosine triphosphate (ATP). All but (j) are hydrolysis reactions.

- Mechanisms 2
  - Pg. 174

f



g Metal ion assisted intramolecular hydrolysis of glycylglycine

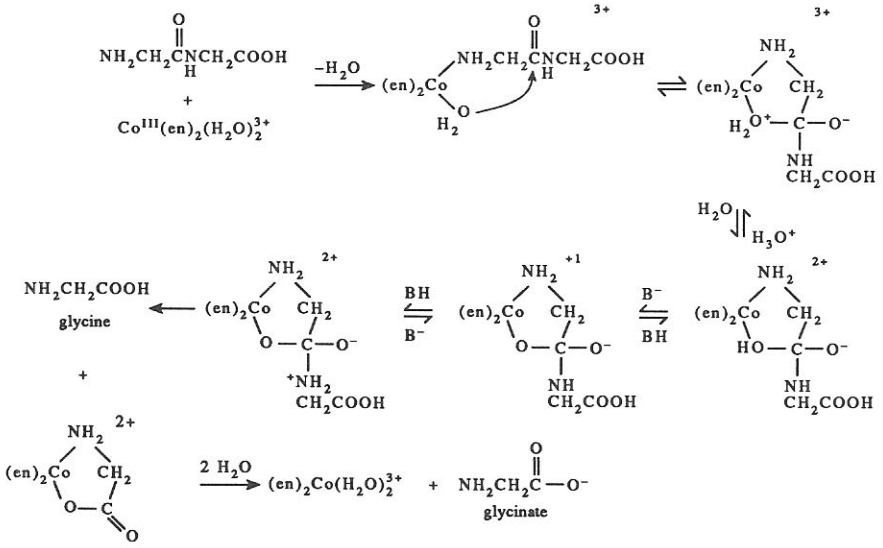
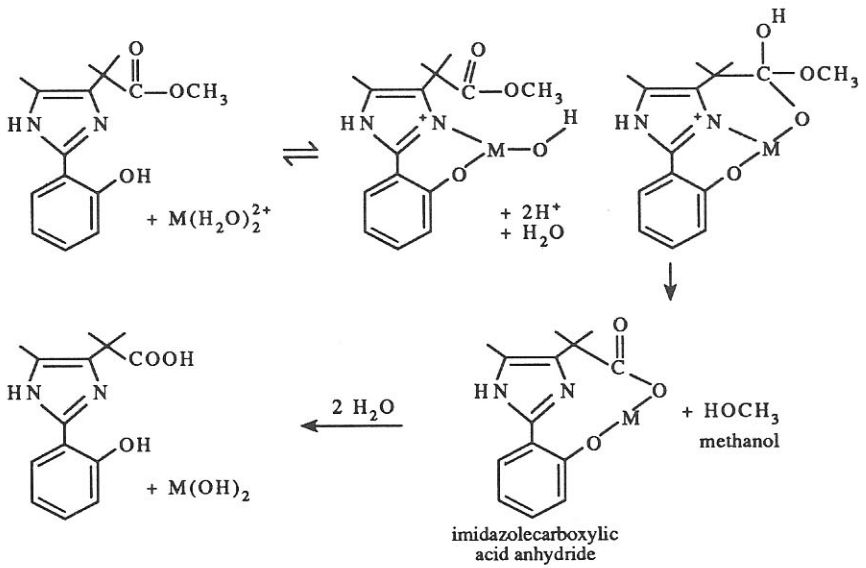


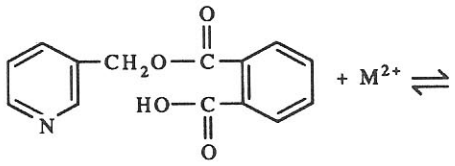
Figure 4-1 (continued).

- Mechanisms 3
  - Pg.175

h Metal ion assisted hydrolysis of a methyl imidazole



i Ester hydrolysis by metal ion stabilization of transition state



2-pyridylmethyl hydrogen phthalate

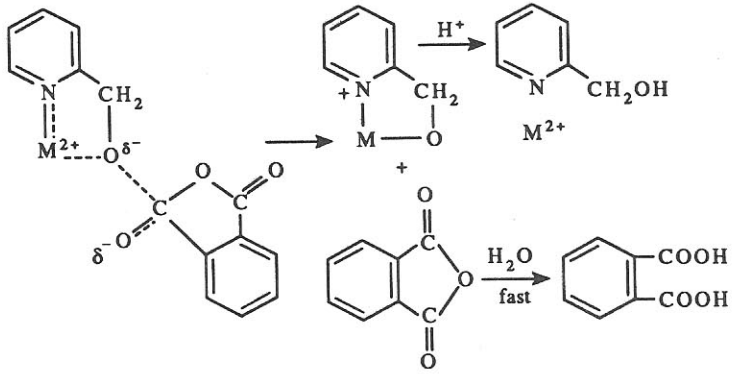
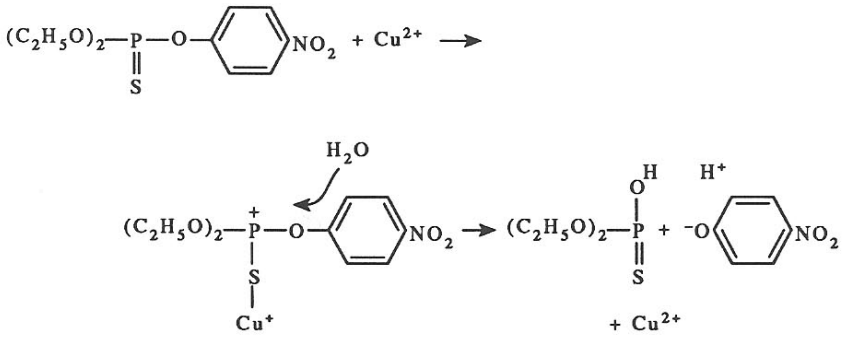


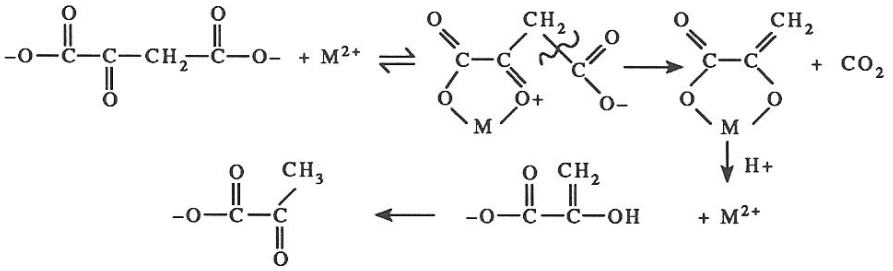
Figure 4-1 (continued).

- Mechanisms 4
  - Pg.176

j Cu(II) assisted hydrolysis of parathion



k Decarboxylation of oxaloacetate



l Metal ion-catalyzed hydrolysis of ATP

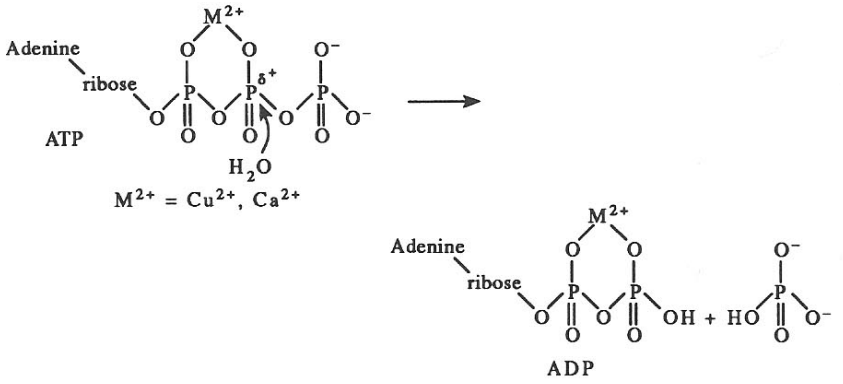


Figure 4-1 (continued).

- To next lecture