Print version

CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #12

Prediction Methods: QSAR, LFERs
Brezonik, pp.553-578

David A. Reckhow | Introduction

Mixed Second Order $\quad A + B \xrightarrow{\ k_2\ } products$

2

□ **Two different reactants**

$$rate \equiv \frac{1}{V}\frac{d\xi}{dt} \equiv \frac{1}{v_A}\frac{d[A]}{dt} =$$

$$\boxed{\begin{aligned}\frac{dx}{dt} &= k_2[A][B] \\ &= k_2\big([A]_0 - x\big)\big([B]_0 - x\big)\end{aligned}}$$

equ 2.17-2.19
in Brezonik

- ◻ Initial Concentrations are different; $[A]_0 \neq [B]_0$
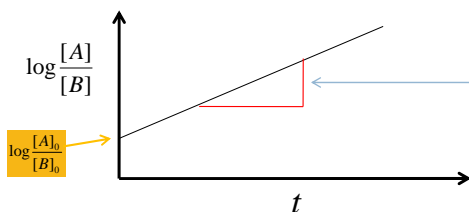
  - ■ The integrated form is:

    $$\frac{1}{[A]_0 - [B]_0}\ln\frac{[B]_0[A]}{[A]_0[B]} = k_2 t$$

    Similar to equ
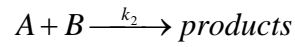   9.18 in Clark

  - ■ Which can be expressed as:

    $$\log\frac{[A]}{[B]} = 0.43 k_2\big([A]_0 - [B]_0\big)t - \log\frac{[B]_0}{[A]_0}$$

$\log\dfrac{[A]}{[B]}$

$\log\dfrac{[A]_0}{[B]_0}$

t

CEE 697K Lecture #12   David A. Reckhow

Mixed Second Order

$$A + B \xrightarrow{k_2} products$$

3

- Initial Concentrations are the same; $[A]_0 = [B]_0$

$$[A] = [B] = [A]_0 - x = [B]_0 - x$$

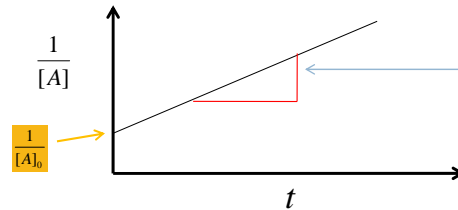$$\frac{dx}{dt} = k_2[A][A]$$
$$= k_2([A]_0 - x)([A]_0 - x)$$

- The integrated form is:

$$\int \frac{d[A]}{[A]^2} = \int \nu_A k_2 dt \quad \Rightarrow \quad \frac{1}{[A]} - \frac{1}{[A]_0} = 2k_2 t$$

- Which can be integrated:

$$\frac{1}{[A]} = 2k_2 t + \frac{1}{[A]_0}$$

$\frac{1}{[A]}$
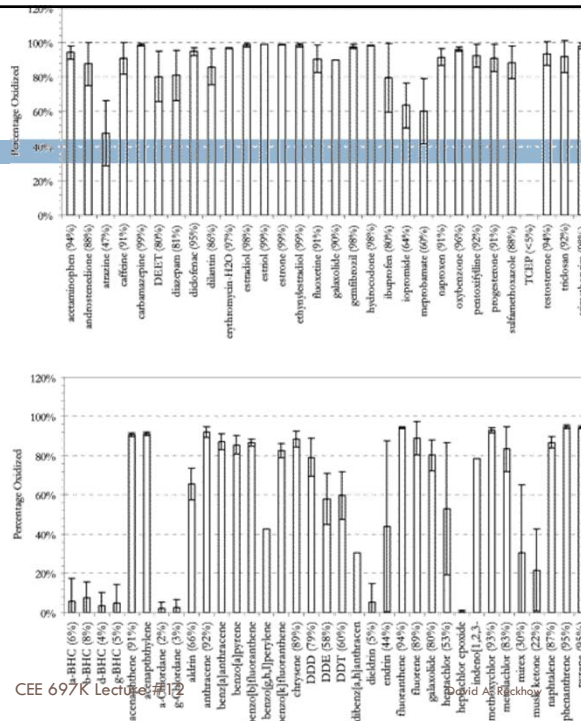
$\frac{1}{[A]_0}$

t

CEE 697K Lecture #12

David A. Reckhow

TOrCs

4

- A few PPCPs
  - Removal by ozone
- Problem
  - ~9,000,000 organic compounds known
  - About 80,000 in common use
  - Many more are present as unwanted byproducts

Westerhoff et al., 2005 [EST 39:17:6649]   CEE 697K Lecture #12   David A. Reckhow

Kinetic Prediction Methods

□ Types

  ◘ Based on properties

  ▪ QPAR: Quantitative Property-Activity Relationships

    ▪ e.g., predicting bioaccumulation from K_{ow}

  ▪ QPPR: Quantitative Property-Property Relationships

    ▪ e.g., predicting K_{ow} from chromatographic retention time (k')

  ◘ Based on structure

  ▪ QSAR: Quantitative Structure-Activity Relationships

    ▪ e.g., rate constants from ring substituents

  ▪ QSPR: Quantitative Structure-Property Relationships

    ▪ e.g., solubility from ionic radius

CEE 697K Lecture #12   David A. Reckhow

LFERs

□ Linear Free Energy Relationships

  ◘ Theoretical Basis

  ▪ Kinetics are correlated to thermodynamics for a given "type" of reaction

  $$\frac{\Delta G^{\neq}}{\Delta G^{o}} \approx const.$$

  ◘ Types

  ▪ Bronsted: acid/base catalyzed reactions

  ▪ Hammett: aromatic and alkene reactions

  ▪ Taft: aliphatic reactions

  ▪ Marcus: metal redox reactions
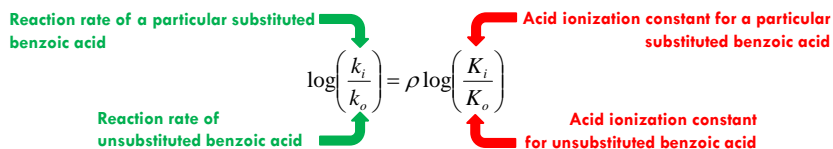
CEE 697K Lecture #12   David A. Reckhow

Hammett Equation I

- Developed in 1930s to explain substituent effects on rates of meta and para substituted benzene compounds
- Reaction rates depend on substituent and position and effect is similar from one reaction to another

Reaction rate of a particular substituted benzoic acid

Acid ionization constant for a particular substituted benzoic acid

$$\log\left(\frac{k_i}{k_o}\right) = \rho \log\left(\frac{K_i}{K_o}\right)$$

Reaction rate of unsubstituted benzoic acid

Acid ionization constant for unsubstituted benzoic acid

- And $\quad \sigma_i \equiv \log\left(\frac{K_i}{K_o}\right)$

- So: $\quad \log\left(\frac{k_i}{k_o}\right) = \rho\sigma$

Because the ion recombinations (benzoate + proton) are diffusion controlled, they all occur at about the same rate. This makes k_f directly proportional to K, and results in ρ =1.0 for benzoic acid dissociation.

CEE 697K Lecture #12

David A. Reckhow

Hammett Equation II

- Substituent & Reaction Constants
  - Meaning
    - Substituent constants are a measure of changes in electron density at the reactive site as a result of the presence of the substituent
      - As $\sigma \uparrow$, e^- density $\downarrow$
  - Source of Constants
    - Table 7-3A for substituent constants (σ)
    - Table 7-3B for reaction constants (ρ)
  - Effects of meta and para substituents are additive
  - Not applicable to ortho substituents due to large steric affects
- Reactions which Hammett Equation applies
  - Hydrolysis
  - Aromatic substitution
  - Oxidation
  - Enzyme catalyzed reactions

CEE 697K Lecture #12

David A. Reckhow

Substituent Constants

9

- Values from Brezonik
  - Table 7-3
    - (pg. 563)
- Meaning
  - $\sigma > 0$
    - Electron withdrawing
  - $\sigma < 0$
    - Electron donating

Substituent	σ_p	σ_m	σ_p+	σ+$_m$	σ^*
-NH$_2$	-0.66	-0.15			0.1
-OH	-0.35	0.08			0.25
-OCH$_3$	-0.26	0.08	-0.76	0.05	0.25
-CH$_3$	-0.16	-0.07	-0.31	-0.06	-0.05
-C$_6$H$_5$	-0.01	0.06	-0.18	0.11	0.1
-H	0	0	0	0	0
-F	0.08	0.35	-0.07	0.35	0.52
-Cl	0.23	0.37	0.11	0.4	0.47
-Br	0.23	0.39	0.15	0.41	0.45
-I	0.28	0.35	0.14	0.36	0.39
-CN	0.68	0.62	0.66	0.56	0.58
-CH$_3$SO$_2$	0.71	0.65			0.59
-NO$_2$	0.79	0.71	0.79	0.67	0.63

$$\log\left(\frac{k_i}{k_o}\right) = \rho\sigma$$

CEE 697K Lecture #12

David A. Reckhow

Reaction Constants

10

- Values from Brezonik
  - Table 7-3
    - (pg. 563)
- Meaning
  - $\rho > 0$
    - Nucleophilic reaction
    - Hindered by high electron density
  - $\rho < 0$
    - Electrophilic reaction
    - Accelerated by high electron density

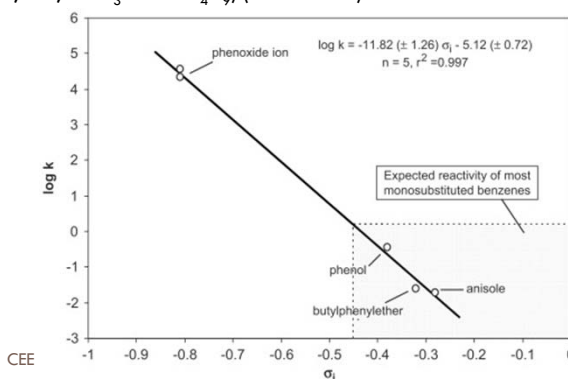| Reactions	ρ	ρ^*	δ
ionization of benzoic acids	1.00		
OH- catalyzed hydrolysis of ethylbenzoates	2.55		
Methlation of benzoic acids	-0.58		
Ionization of carboxylic acids		1.72	
Alkaline hydrolysis of Co(NH$_3$)$_5$O$_2$CR^{+2} in water		0.79	
Catalysis of nitraminde decomposition by RCOO-		-1.43	
Acid hydrolysis of formals, CH$_2$(OR)$_2$		-4.17	
Alkaline hydrolysis of primary amides		1.60	
ionization of orthobenzoic acids		1.79	
Hydrolysis of bromoalkanes		-11.9	
Acid dissociation constants of aldehyde-bisfulites		-1.29	
Alkaline hydrolysis of diphthalate esters		4.59	1.52
Acid hydrolysis of orthobenzamides			0.81
Acid methanolysis of 2-naphthyl esters			1.38
Methyl iodide reaction with alkylpyridines			2.07

$$\log\left(\frac{k_i}{k_o}\right) = \rho\sigma$$

CEE 697K Lecture #12

David A. Reckhow

Hammett Relationship

11

- Mono-substituted aromatics and HOCl
  - Assumed $\sigma_i \approx \sigma_{ortho} \approx \sigma_{para}$
  - second-order rate constants for the reaction of phenoxide ion, phenol, anisole and butylphenylether with HOCl versus the estimated Hammett constants of the substituents on benzene (O^-, OH, OCH_3 and OC_4H_9) (T 22–25 °C).

From: Deborde & von Gunten, 2008 [Wat. Res. 42(1)13]
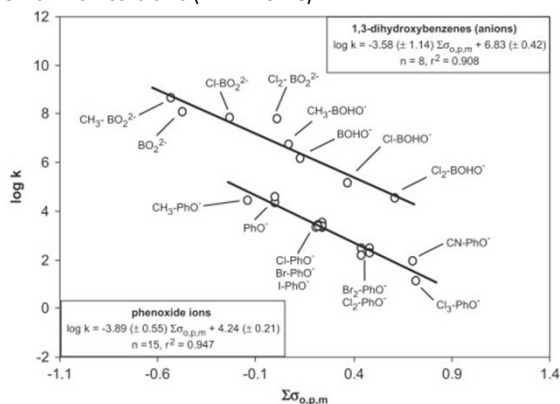
CEE

Hammett Relationship

12

- Poly-substituted aromatics and HOCl
  - Cross-linear correlation between the second-order rate constants for the reactions of substituted phenoxide ions (PhO^-) and 1,3-dihydroxybenzene anions ($BOHO^-$ and BO_2^{2-}) with HOCl and the Hammett constants (T 22–25 °C).
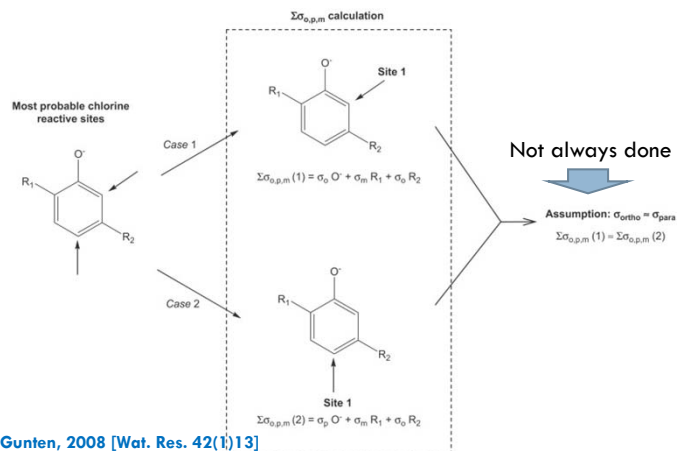 - Assumed $\sigma_{ortho} \approx \sigma_{para}$

Large negative slope (-3.6 to -3.9) indicates electrophilic nature of this reaction

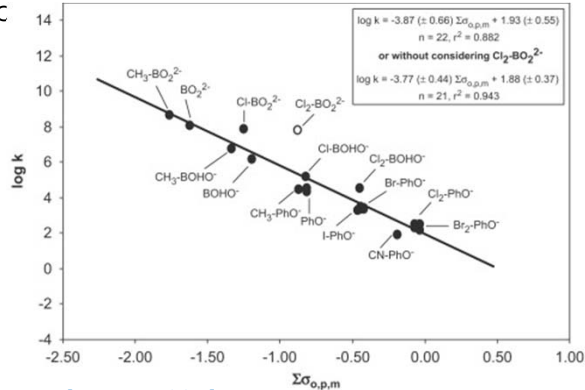**From:** Deborde & von Gunten, 2008 [Wat. Res. 42(1)13]

Calculation of sigma

13

- Example of $\sum\sigma_{o,p,m}$ calculation for the corrected Hammett-type correlation

Not always done

From: Deborde & von Gunten, 2008 [Wat. Res. 42(1)13]

CEE 697K Lecture #12

David A. Reckhow

Combined Hammett plot

14

- Corrected Hammett-type correlation of log k versus $\sum\sigma_{o,p,m}$ (determined from substituent position to the most probable chlorine reactive site) for the reaction of HOCl with phenoxide ions (PhO$^-$), 1,3-dihydroxybenzene anions (BOHO$^-$ and BO$_2{}^{2-}$) (T 22–25 °C

From: Deborde & von Gunten, 2008 [Wat. Res. 42(1)13]

CEE 697K Lecture #12

David A. Reckhow

Components

- Composition
  - Resonance (R)
  - Field (F) or Inductive
- Relationship

$$\sigma_p \approx R + F$$

$$\sigma_m \approx 0.3R + 1.1F - 0.03$$

Substituent	σ_p	σ_m	σ_p+	$\sigma+_m$	σ^*	R	F
-N(CH₃)₂	-0.83	-0.16	-1.70			-0.98	0.15
-NH₂	-0.66	-0.15			0.10	-0.74	0.08
-OH	-0.35	0.08			0.25	-0.70	0.33
-OCH₃	-0.26	0.08	-0.76	0.05	0.25	-0.56	0.29
-C(CH₃)₃	-0.20	-0.10	-0.26			-0.18	-0.02
-CH₃	-0.16	-0.07	-0.31	-0.06	-0.05	-0.18	0.01
-CH(CH₃)₂	-0.15	-0.04	-0.28			-0.19	0.04
-CH₂C₆H₅	-0.09	-0.08	-0.28			-0.05	-0.04
-CH=CHC₆H₅	-0.07	0.03	-1.00			-0.17	0.10
-CH=CH₂	-0.04	0.06	-0.16			-0.17	0.13
-OC₆H₅	-0.03	0.25	-0.50			-0.40	0.37
-C₆H₅	-0.01	0.06	-0.18	0.11	0.10	-0.13	0.12
-H	0	0	0	0	0	0	0
-NHCOCH₃	0.00	0.21	-0.60			-0.31	0.31
-F	0.08	0.35	-0.07	0.35	0.52	-0.39	0.45
-Cl	0.23	0.37	0.11	0.40	0.47	-0.19	0.42
-Br	0.23	0.39	0.15	0.41	0.45	-0.22	0.45
-I	0.28	0.35	0.14	0.36	0.39	-0.24	0.42
-CONH₂	0.36	0.28				0.10	0.26
-CHO	0.42	0.35	0.73			0.09	0.33
-COC₆H₅	0.43	0.34	0.51			0.12	0.31
-COOCH₃	0.45	0.36	0.49			0.11	0.34
-COCH₃	0.50	0.38				0.17	0.33
-CN	0.68	0.62	0.66	0.56	0.58	0.15	0.51
-CH₃SO₂	0.71	0.65			0.59		
-NO₂	0.79	0.71	0.79	0.67	0.63	0.13	0.65

CEE 697K Lecture #12   David A. Reckhow

Other types of reactions

- Reactions involving carbonium ions or carbanion intermediates
  - Need to use $\sigma+$ values (σ_p+, σ_m+)
  - These were determined from hydrolysis of m– and p– substituted 2–chloro–phenylpropanones

CEE 697K Lecture #12   David A. Reckhow

Others

- Taft relationship
  - Includes electronic and steric effects
  - Applied mostly to aliphatics
    - Therefore resonance isn't important

CEE 697K Lecture #12

David A. Reckhow

Taft Substituent Constants

- From Schwarzenbach et al., 1993
  - Environmental Organic Chemistry

TABLE 12.4 Examples of Taft Polar and Steric Substituent Constant for Aliphatic Systems[a]

Substituent	σ^*	E_s	Substituent	σ^*	E_s
—H	0.49	1.24	—CH$_2$C$_6$H$_5$	0.22	−0.38
—CH$_3$	0.00	0.00	—CH$_2$CH$_2$C$_6$H$_5$	0.08	−0.38
—C$_2$H$_5$	−0.10	−0.07	—CH$_2$F	1.10	−0.24
—n-C$_3$H$_7$	−0.12	−0.36	—CHF$_2$	2.05	−0.67
—i-C$_3$H$_7$	−0.19	−0.47	—CH$_2$Cl	1.05	−0.24
—n-C$_4$H$_9$	−0.13	−0.39	—CHCl$_2$	1.94	−1.54
—i-C$_4$H$_9$	−0.13	−0.93	—CCl$_3$	2.65	−2.06
—s-C$_4$H$_9$	−0.21	−1.13	—CH$_2$CH$_2$Cl	0.39	−0.90
—t-C$_4$H$_9$	−0.30	−1.54	—CH$_2$Br	1.00	−0.27
—cyclo-C$_6$H$_{11}$	−0.15	−0.79	—CHBr$_2$		−1.86
—CH$_2$-cyclo-C$_6$H$_{11}$	−0.06	−0.98	—CBr$_3$		−2.43
—CH=CH$_2$	0.36	−1.63	—CH$_2$OCH$_3$	0.52	−0.19
—C$_6$H$_5$ (phenyl)	0.60	−2.55	—CH$_2$OC$_6$H$_5$	0.85	−0.33

[a]Data taken from a more comprehensive data set given by Williams (1984).

adding a steric term, it is postulated that

$$\log\left(\frac{k}{k_{ref}}\right) = \rho^*\sigma^* + \delta E_s \qquad (12\text{-}29)$$
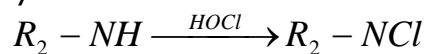
N-chloro-organics

- Reactions of chlorine with organic amines
  - Primary amines

$$R - NH_2 \xrightarrow{\ HOCl\ } R - NHCl \xrightarrow{\ HOCl\ } R - NCl_2$$

  - Secondary amines

$$R_2 - NH \xrightarrow{\ HOCl\ } R_2 - NCl$$

- Inorganic chloramines can transfer their active chlorine in a similar fashion

CEE 697K Lecture #2

David A. Reckhow

Taft Plot

- Formation of organic chloramines

secondary amines   primary amines

log k = 1.14 (± 0.26) σ* + 7.24 (± 0.17)
n = 14, r² = 0.884

tertiary amines
log k = -2.24 (± 0.82) σ* + 4.92 (± 0.32)
n = 7, r² =0.907

Taft's correlation for chlorination of basic aliphatic amines at 25 °C: Full symbols (●) represent rate constant values used by Abia et al. (1998) and were used for calculation of correlation coefficients and Taft's plot equations; open circles (○) represent other rate constants reported in literature

From: Deborde & von Gunten, 2008 [Wat. Res. 42(1)13]

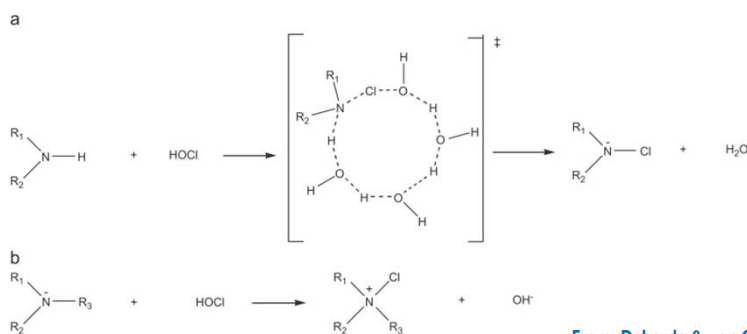CEE 697K Lecture #12

David A. Reckhow

Interpretation

- Reaction schemes proposed by <u>Abia et al. (1998)</u> for the chlorination of organic aliphatic amines: (a) primary and secondary amines; (b) tertiary amines.
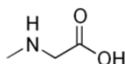

From: Deborde & von Gunten, 2008 [Wat. Res. 42(1)13]

CEE 697K Lecture #12

David A. Reckhow

Degradation of Organic Chloramines

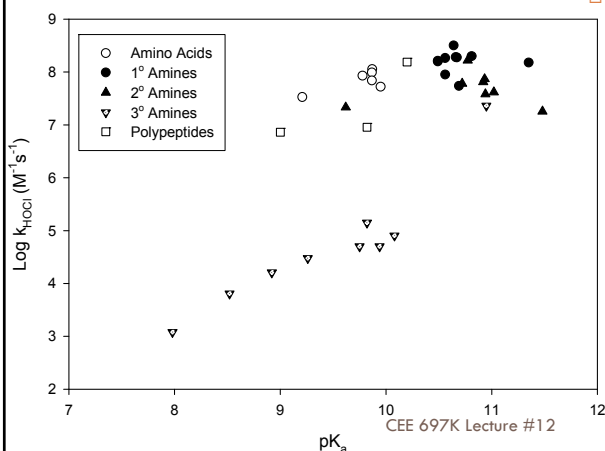| Parent Amine	k_{obs} (s^{-1})	$t_{1/2}$ (min)
Alanine	1.3E-04	86
Glycine	1.4E-06	8400
Histidine	2.7E-04	43
Leucine	1.6E-04	72
Phenylalanine	2.2E-04	52
Serine	2.4E-04	49
Creatinine	3.5E-06	3300
Glycine N acetyl	6.0E-07	19000
Glycine ethyl ester	2.3E-04	50
Glycylglycine	1.0E-05	1100
Sarcosine	5.3E-05	210

CEE 697K Lecture #12

David A. Reckhow

QSPRs

- **Relationship between basicity and 2nd order rate constants for reaction of HOCl with N-compounds**
  - *Data Sources:* Friend, 1956; Hussain et al., 1972; Isaac et al., 1983; Armesto et al., 1993; Armesto et al., 1994; Antelo et al., 1995; Abia et al., 1998
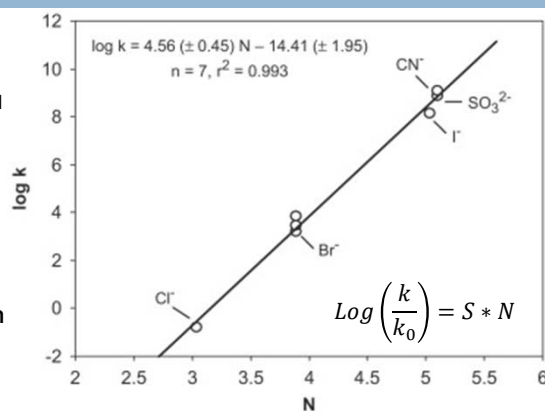
CEE 697K Lecture #12

David A. Reckhow

QPAR: Rate Constants vs Nucleophilicty

- Nucleophilicity
  - Tendency to donate a pair of electrons
  - Closely aligned with Basicity
    - Tendency to donate a pair of electrons to an H atom/ion

$$Log\left(\frac{k}{k_0}\right) = S * N$$

Swain–Scott plot of log k for the reaction of HOCl with Cl⁻, Br⁻, I⁻, SO$_3^{2-}$ and CN⁻ versus the nucleophilicity (N) of the anions at 25 °C. Adapted from Gerritsen and Margerum (1990).

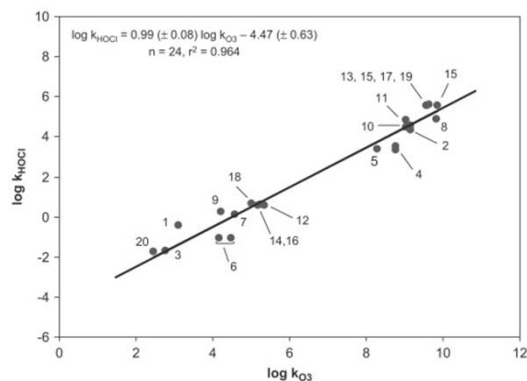**From: Deborde & von Gunten, 2008 [Wat. Res. 42(1)13]**

CEE 697K Lecture #12

David A. Reckhow

QAAR I

25

- Linear correlation between the log k_{HOCl} and log k_{O3} for selected aromatic compounds (mostly phenols) for which electrophilic chlorine and ozone attack is expected..

$$\log k_{HOCl} = 0.99 \, (\pm 0.08) \log k_{O3} - 4.47 \, (\pm 0.63)$$
$$n = 24, \, r^2 = 0.964$$

No.	Compounds
1	Phenol
2	Phenoxide ion
3	4-chlorophenol
4	4-chlorophenoxide ion
5	2-chlorophenoxide ion
6	4-methylphenol
7	4-n-nonylphenol
8	4-n-nonylphenol (ionized)
9	Bisphenol A
10	Bisphenol A (ionized 1)
11	Bisphenol A (ionized 2)
12	Estradiol
13	Estradiol (ionized)
14	17-ethinylestradiol
15	17-ethinylestradiol (ionized)
16	Estrone
17	Estrone (ionized)
18	Estriol
19	Estriol (ionized)
20	Anisole

CEE 697K Lecture #12

David A. Reckhow

QAAR II

26

- Decarboxylation and metal complexation
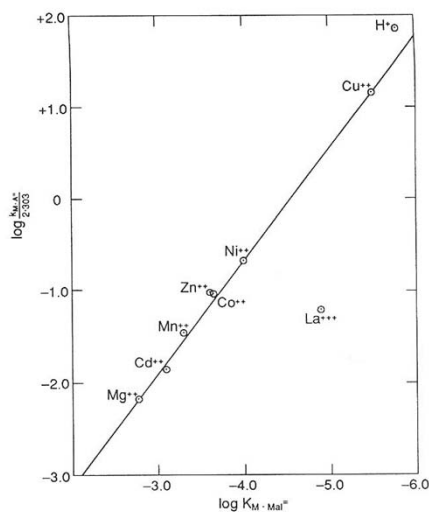 - Malonic acid's reaction with various metals

Figure 4-2. The rate constant, k, for metal-catalyzed decarboxylation of malonic acid (acetonedicarboxylic acid) is correlated with K_{MMa}, the dissociation constant for corresponding metal-malonate complex — a linear free-energy relationship. [From Prue, J.E., *J. Chem. Soc.*, II, 2331 (1952). With permission.]
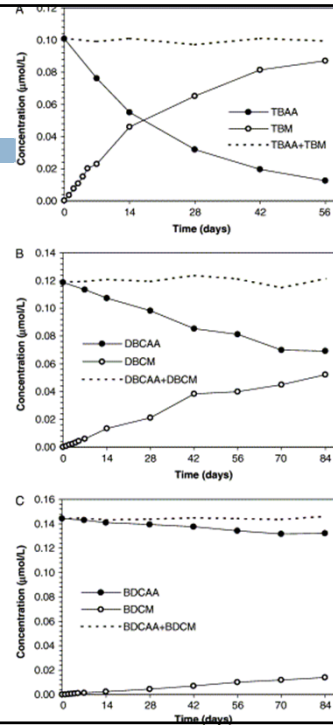
Abiotic Loss of HAAs

27

□ Study of Trihaloacetic Acids

■ Zhang and Minear, 2002

■ Water Research 36:3665-3673

The decomposition of THAAs and the formation of THMs in MilliQ water buffered at pH 7 and 23°C with an initial concentration of 30 µg/L of (A) TBAA, (B) DBCAA, (C) BDCAA, respectively
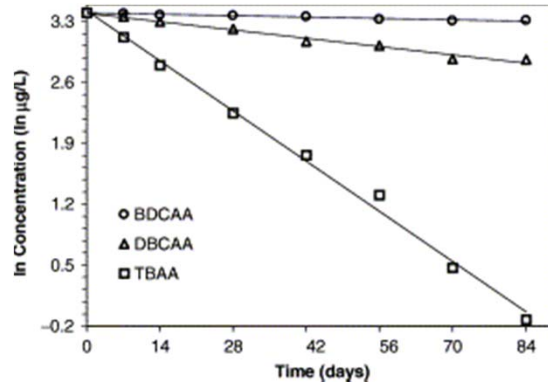
CEE 697K Lecture #12

Abiotic Loss of TriHAAs II

28

□ The decomposition of THAAs in MilliQ water buffered at pH 7 and 23°C with an initial concentration of 30 µg/L of each species.

From: Zhang & Minear, 2002

CEE 697K Lecture #12

David A. Reckhow

14

Abiotic Loss of TriHAAs III

29

□ Rate constants and r^2 values

	23°C 30 µg/L[a] k (day^{-1})[b]	R^2 [c]	23°C 10 µg/L k (day^{-1})	R^2	23°C 5 µg/L k (day^{-1})	R^2
BDCAA	0.0012	0.969	0.0011	0.976	0.0011	0.995
DBCAA	0.0068	0.994	0.0062	0.998	0.0056	0.993
TBAA	0.0412	0.988	0.0400	0.998	0.0379	0.985

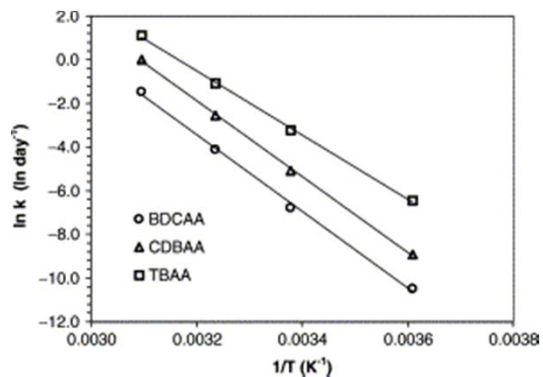|	4°C 30 µg/L k (day^{-1})	R^2	36°C 30 µg/L k (day^{-1})	R^2	50°C 30 µg/L k (day^{-1})	R^2
BDCAA	0.000028	0.982	0.0165	0.990	0.234	0.994
DBCAA	0.000135	0.989	0.0783	0.997	1.02	0.999
TBAA	0.00158	0.990	0.344	0.988	3.02	0.988

From: Zhang & Minear, 2002

CEE 697K Lecture #12

David A. Reckhow

Abiotic Loss of TriHAAs IV

30

□ Arrhenius plot of the decomposition of THAAs in MilliQ water buffered at pH 7.
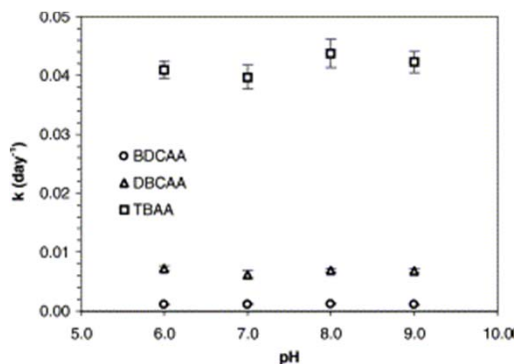

From: Zhang & Minear, 2002

CEE 697K Lecture #12

David A. Reckhow

Abiotic Loss of TriHAAs V

- □ The effect of pH on the decomposition of THAAs in MilliQ water buffered with 5 mM phosphate at 23°C
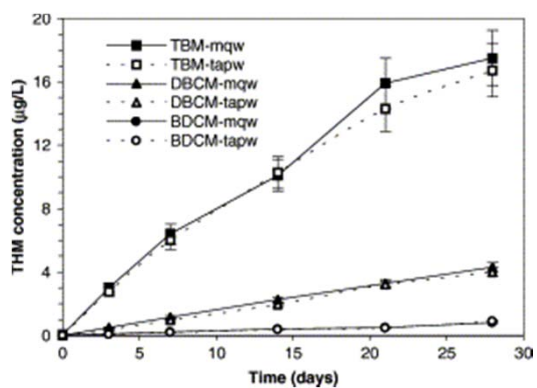
CEE 697K Lecture #12   David A. Reckhow

Abiotic Loss of TriHAAs VI

- □ The formation of THMs in MilliQ water and tap water without buffer at 23°C with an initial concentration of 30 µg/L of each THAA (control subtracted)
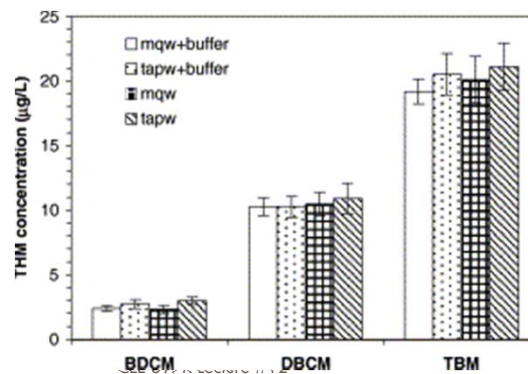
David A. Reckhow

Abiotic Loss of TriHAAs VII

33

- Formation of THMs in MilliQ water and tap water with or without buffer at 50°C with an initial concentration of 30 μg/L of each THAA after 11 h (control subtracted).

From: Zhang & Minear, 2002

David A. Reckhow

Zhang & Minear Study

34

- Final Compiled Rates for the THAAs

	k (day^{-1})	Es^a	$\ln(k)$	$t_{1/2}$ (day)
TFAA	$6.16 \times 10 - 11$	-1.38	-23.51	1.12×1010
TCAA	0.00032	-2.91	-8.06	2190
BDCAA	0.0011	-3.10	-6.81	630
DBCAA	0.0062	-3.29	-5.08	112
TBAA	0.040	-3.48	-3.22	17
DCIAA[b]				
BCIAA[b]				
DBIAA[b]				
CDIAA[b]				
BDIAA[b]				
TIAA[b]				

?

From: Zhang & Minear, 2002

CEE 697K Lecture #12

David A. Reckhow

CHO Cytotoxicity

35

□ Work of Michael Plewa

DBP Chemical Class

CHO Cell Cytotoxicity as %C½ Values (~LC_{50})
Log Molar Concentration (72 h Exposure)

CEE 697K Lecture #12

David A. Reckhow

Zhang & Minear model I

36

□ Standard Hammett LFER

$$\log(k_x) = \rho\sigma + \log(k_H)$$

- where k_x is a rate constant, k_H is the rate constant for the parent unsubstituted compound, ρ is a measure of the sensitivity of a reaction to the electronic effect of the substituents X, σ is the parameter for electronic effect

□ Tailoring the substituent constant

- Taft separates the electronic and steric properties of substituents by making use of either the hydrolysis of esters of substituted acetic acids (XCH_2COOR) or the reverse esterification reaction

$$\sigma^* = 0.403[\log(k_x/k_H)_B - \log(k_x/k_H)_A]$$

- where σ^* is the inductive-field effect of X, k_x is the rate constant for the hydrolysis of XCH_2COOR, k_H is that for the hydrolysis of the parent CH_3COOR ($\sigma^* = 0$ for CH_3, where X = H), B and A indicate hydrolysis in basic or acid solution, respectively

From: Zhang & Minear, 2002

CEE 697K Lecture #12

David A. Reckhow

Zhang & Minear model II

37

□ Earlier studies of the Hammett equation showed that the electronic effect of substituents on acid hydrolysis was nil, but the effect of substituents on basic hydrolysis of benzoate esters was significant. Taft defines the second term in the previous equation as a steric parameter: $E_s = \log(k_x/k_H)_A$. Substituting E_s into

$$\sigma^* = 0.403[\log(k_x/k_H)_B - E_s] \qquad \text{or} \qquad \log(k_x)_B = E_s + 2.48\sigma^* + \log(k_H)_B.$$

□ Hansch and Leo presented an equation for the general approach to correlating rate constants that involve steric and electronic effects:

$$\log(k) = aE_s + b\sigma + d$$

  ▪ where $\sigma = \sigma_I + \sigma_R$, σ_I and σ_R represent inductive and resonance components of electronic effect. k is reaction rate constant. a, b and d are constants

From: Zhang & Minear, 2002

CEE 697K Lecture #12   David A. Reckhow

Zhang & Minear model III

38

□ In trihaloacetic acids, since substituents (F, Cl, Br, I) do not accept or donate a pair of electrons that are in direct conjugation with the reaction center, σ_R values are negligible. The values of σ_I (F 0.45, Cl 0.42, Br 0.45, I 0.42) are very close to one another, σ_I may be considered as a part of d. Therefore, the previous equation is simplified to

$$\ln(k) = mE_s + n$$

  ▪ where m and n are constants.

□ The values of E_s for substituents of F, Cl, Br are −0.46, −0.97, −1.16 and −1.40, respectively. If E_s for a THAA is assumed to be the sum of E_s of three single substituents (Xi) in it:

$$E_s(\text{THAA}) = \Sigma E_s(\text{Xi}) \ \text{Xi} = \text{F,Cl,Br, orI.}$$

From: Zhang & Minear, 2002   CEE 697K Lecture #12   David A. Reckhow
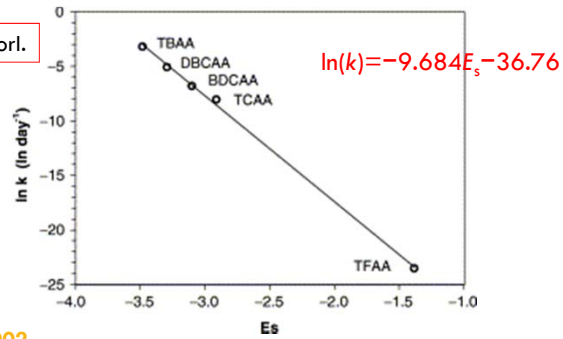
Zhang & Minear model IV

39

□ LFER Model - correlation

- where k is the decomposition rate constant of a THAA in water at 23°C, E_s is the value of steric effect of the THAA calculated according to
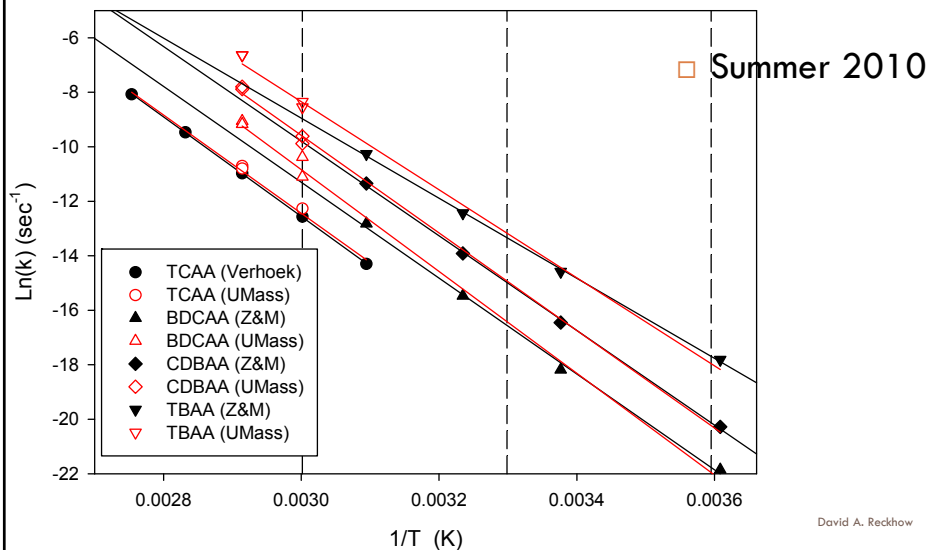
$E_s(THAA)=\Sigma E_s(Xi)$ Xi=F,Cl,Br, orl.

$\ln(k)=-9.684E_s-36.76$

From: Zhang & Minear, 2002

CEE 697K Lecture #12

David A. Reckhow

UMass Studies

40

□ Summer 2010

David A. Reckhow

Re-assessment

41

□

Lnk (sec^{-1}) vs Es plot

- ○ Pooled Data @20C
- × Z&M Data @20C
- ● Z&M Data @23C w/TFA

Br$_3$
Br$_2$Cl
BrCl$_2$
Cl$_3$

Half-life (hr): 10, 100, 1000, 10000, 100000

-10, -12, -14, -16, -18, -20

-4.0, -3.8, -3.6, -3.4, -3.2, -3.0, -2.8

Es

Zhang & Minear model V

42

□ Final calculation

	k (day^{-1})	Es[a]	$\ln(k)$	$t_{1/2}$ (day)
TFAA	$6.16 \times 10 - 11$	-1.38	-23.51	1.12×1010
TCAA	0.00032	-2.91	-8.06	2190
BDCAA	0.0011	-3.10	-6.81	630
DBCAA	0.0062	-3.29	-5.08	112
TBAA	0.040	-3.48	-3.22	17
DCIAA[b]	0.012	-3.34	-4.42	57
BCIAA[b]	0.076	-3.53	-2.58	9.1
DBIAA[b]	0.48	-3.72	-0.74	1.4
CDIAA[b]	0.78	-3.77	-0.25	0.89
BDIAA[b]	4.9	-3.96	1.59	0.14
TIAA[b]	50	-4.20	3.91	0.014

From: Zhang & Minear, 2002

CEE 697K Lecture #12

David A. Reckhow

43

□ <u>To next lecture</u>

CEE 697K Lecture #12   David A. Reckhow