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CEE 690K

ENVIRONMENTAL REACTION KINETICS

Lecture #3

Rate Expressions: Sequential Reactions

Brezonik, pp.39-58, 240-241

Mechanisms: Haloform Reaction

2

□ Chlorine + acetone

□ Morris & Baum, 1978

□ Brezonik, 1994

Pg 240-241

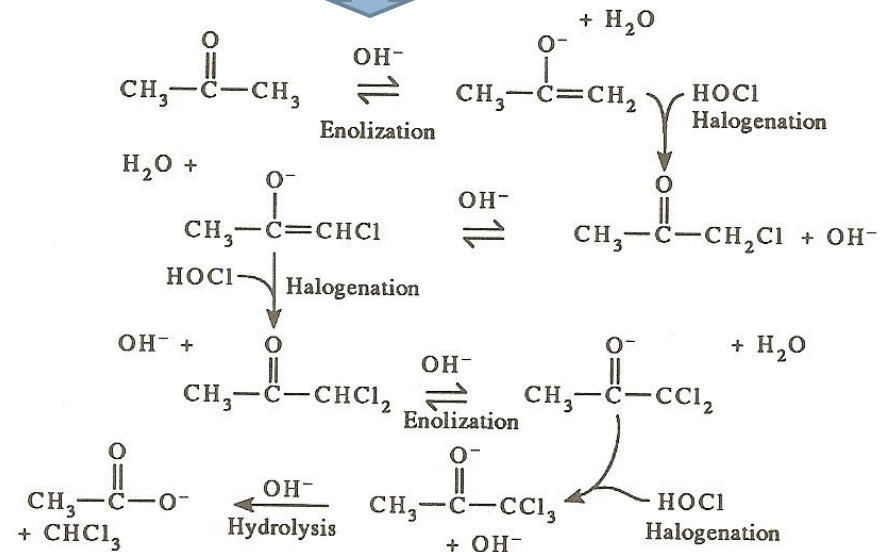
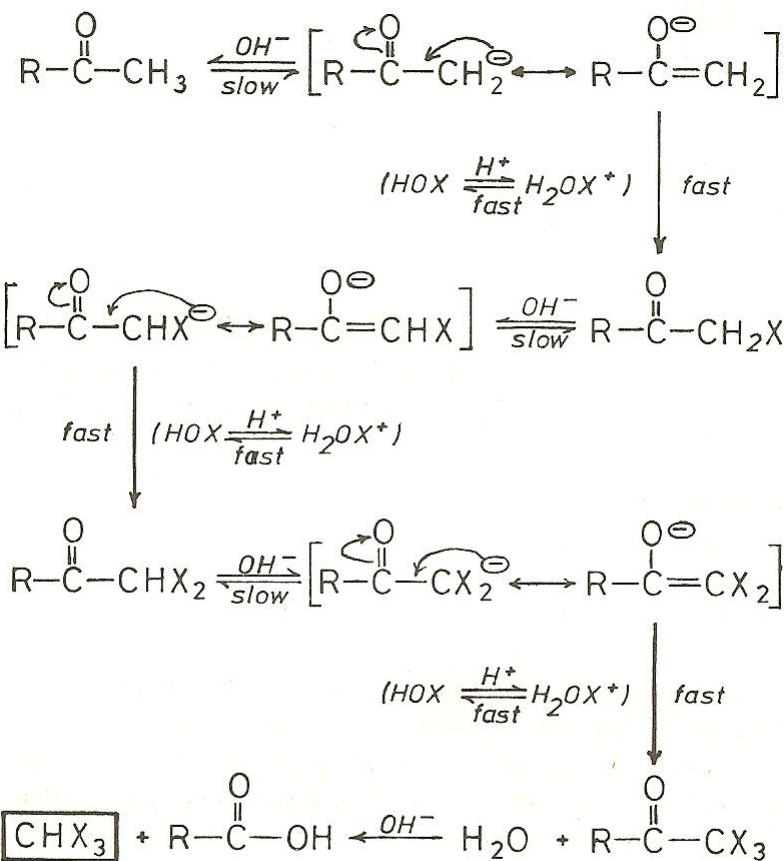


Figure 4-25. Reaction scheme for production of chloroform from acetone by the classic haloform reaction.

Halofrom reaction: initial step

3

- Three potential pathways to enolate
 - ▣ Reaction with water (K_O), hydroxide (K_{OH}), and proton (K_H)
 - $k_f = K_O + K_{OH}[\text{OH}^-] + K_H[\text{H}^+]$
 - For acetone, the OH pathway dominates above pH 5.5

Table I. Rates of Ionization of Ketones^{3,4}

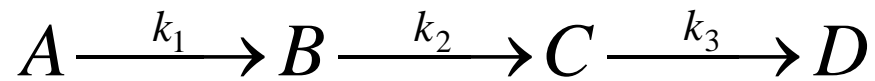
Substance	pK _a	K _O sec ⁻¹	K _{OH} 1/mol, sec	K _H 1/mol, sec	t ₅₀ pH 7, hr	t ₅₀ , pH 8.3 hr
Acetone	20	4.7 x 10 ⁻¹⁰	0.25	2.9 x 10 ⁻⁵	7500	385
Chloroacetone	16.5	5.3 x 10 ⁻⁸	93	6.3 x 10 ⁻⁵	21	1.0
as-Dichloroacetone	15	7.3 x 10 ⁻⁶	450	1.1 x 10 ⁻⁵	3.7	0.21
Pyruvic acid ⁶		4.5 x 10 ⁻⁷				
Ethyl pyruvate ⁶	16	4.7 x 10 ⁻⁷				
Acetylacetone	9.0	1.1 x 10 ⁻²				
Ethyl acetoacetate	10.7	1.2 x 10 ⁻³				
Malonic acid		1.7 x 10 ⁻¹				

$$K_a = \frac{k_f}{k_r} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

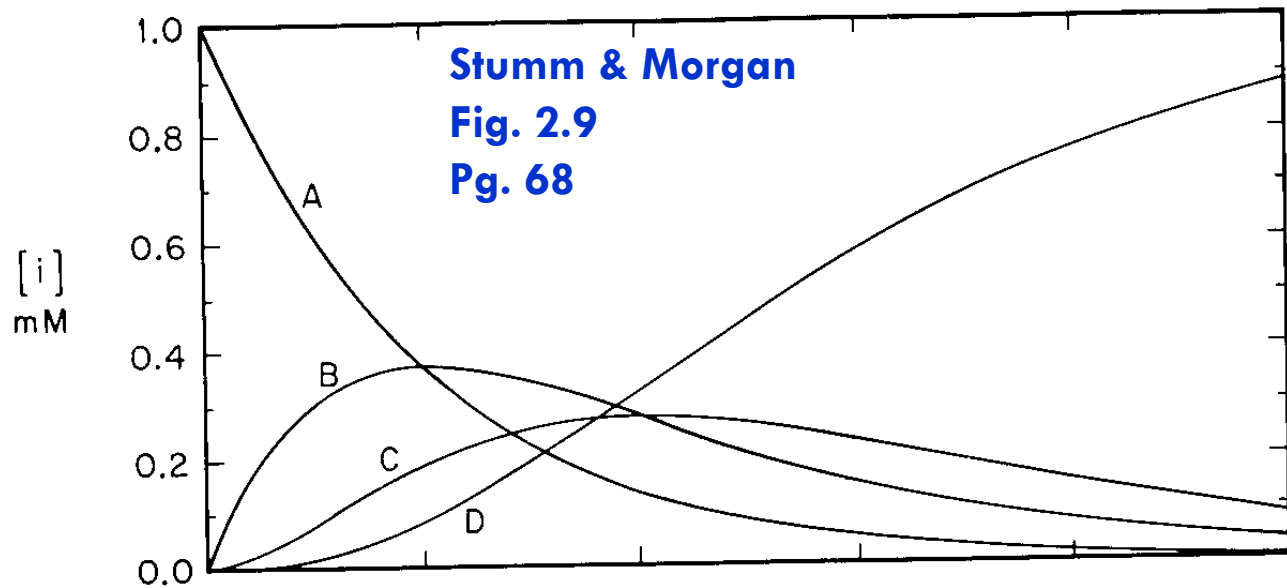
What is k_r ?

Reactions in Series

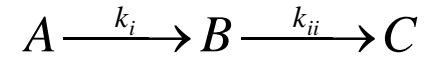
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$$k_1 = k_2 = k_3 = 0.1 \text{ day}^{-1}$$



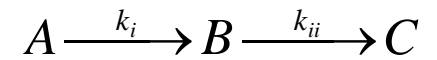
Consecutive Reactions I



5

- Overall rate determined by slowest step
 - If $k_i \gg k_{ii}$
 - A rapidly forms B which then reacts slowly
 - $d[C]/dt \approx k_{ii}[B]$
 - If $k_i \ll k_{ii}$
 - B never builds up; it reacts as soon as it is formed
 - $d[C]/dt \approx k_i[A]$
 - If $k_i \sim k_{ii}$
 - B slowly builds up then disappears
 - Rate must consider both reactions

Consecutive Reactions II



6

□ Writing a separate equation for each species

$$\frac{d[A]}{dt} = -k_i[A]$$

$$\frac{d[B]}{dt} = k_i[A] - k_{ii}[B]$$

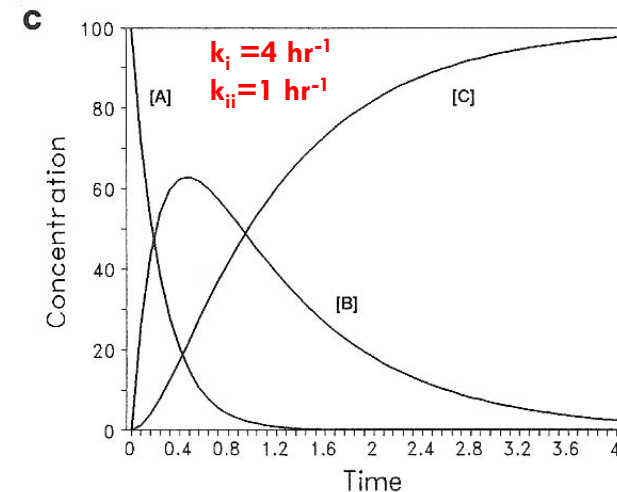
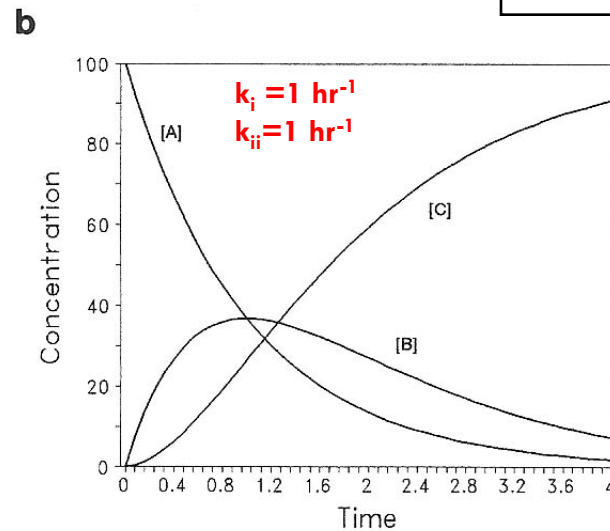
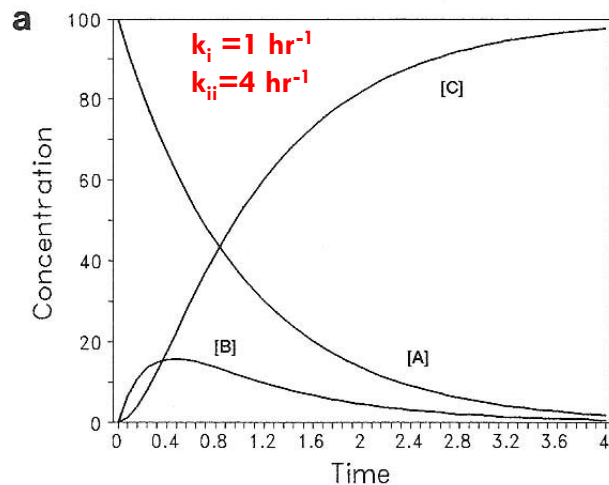
$$\frac{d[C]}{dt} = k_{ii}[B]$$

$$[A] = [A]_0 e^{-k_i t}$$

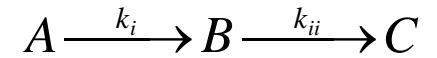
$$[B] = \frac{k_i [A]_0}{k_{ii} - k_i} \left\{ e^{-k_i t} - e^{-k_{ii} t} \right\}$$

$$[C] = \frac{[A]_0}{k_{ii} - k_i} \left\{ k_{ii} (1 - e^{-k_i t}) - k_i (1 - e^{-k_{ii} t}) \right\}$$

Note that this k_i was inadvertently left out of equ. 2-47 in Brezonik

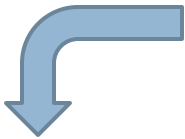


Limiting Cases



7

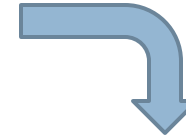
□ If $k_i \gg k_{ii}$



$$[B] = \frac{k_i [A]_0}{k_{ii} - k_i} \left\{ e^{-k_i t} - e^{-k_{ii} t} \right\}$$

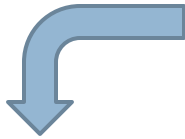
$$[B] = [A]_0 \left\{ e^{-k_{ii} t} \right\}$$

□ If $k_{ii} \gg k_i$



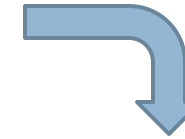
$$[B] = \frac{k_i [A]_0}{k_{ii}} \left\{ e^{-k_i t} \right\}$$

$$[C] = \frac{[A]_0}{k_{ii} - k_i} \left\{ k_{ii} (1 - e^{-k_i t}) - k_i (1 - e^{-k_{ii} t}) \right\}$$



$$[C] = [A]_0 \left\{ -\frac{k_{ii}}{k_i} + (1 - e^{-k_{ii} t}) \right\}$$

$$[C] = [A]_0 (1 - e^{-k_{ii} t})$$



$$[C] = [A]_0 \left\{ (1 - e^{-k_i t}) - \frac{k_i}{k_{ii}} \right\}$$

$$[C] = [A]_0 (1 - e^{-k_i t})$$

Focusing on [B]

8

- Often we are concerned with the maximum concentration of “B”

- ▣ This occurs when $d[B]/dt = 0$

- ▣ And combining this with the general solution for [B]:

$$\frac{d[B]}{dt} = k_i[A] - k_{ii}[B]$$

$$k_i[A] = k_{ii}[B]_{\max}$$

$$[B]_{\max} = \frac{k_i}{k_{ii}}[A]$$
$$= \frac{k_i}{k_{ii}}[A]_0 e^{-k_1 t_{\max-B}}$$

$$t_{\max-B} = \frac{1}{k_i - k_{ii}} \ln\left(\frac{k_i}{k_{ii}}\right)$$

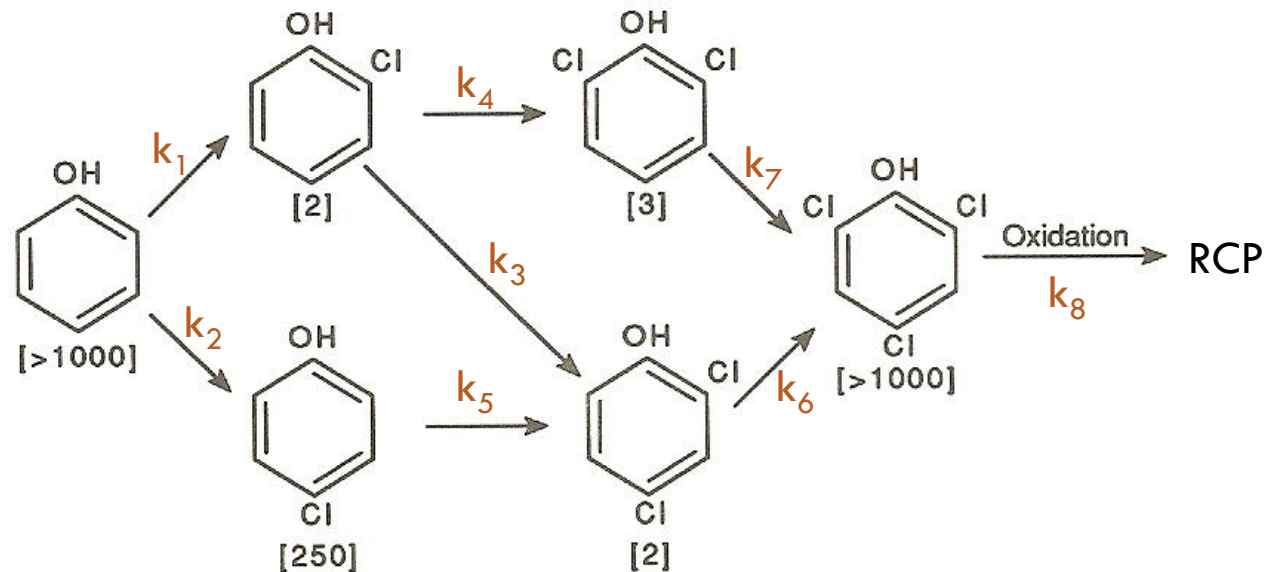
Chlorination of Phenol

9

Table 4-8. Rate Constants (k_{obs}) for Chlorination of Phenols^a

pH	Phenol	2-Chloro-phenol	4-Chloro-phenol	2,4-Dichloro-phenol	2,6-Dichloro-phenol	2,4,6-Tri-chlorophenol
5	2.09E2	4.03E2	9.60E1	2.38E2	6.32E2	1.17E2
6	4.82E2	1.04E3	2.98E2	4.02E2	1.34E3	3.46E2
7	2.23E3	3.16E3	8.93E2	1.76E3	4.95E3	5.16E2
8	6.15E3	8.15E3	1.84E3	2.72E3	2.19E3	1.45E2
9	6.14E3	3.21E3	1.54E3	5.48E2	2.96E2	1.34E1
10	2.84E3	4.30E3	4.15E2	6.32E1	3.09E1	9.05E-1
11	4.73E2	4.60E1	4.70E1	6.37	3.12	5.44E-2
12	4.50E1	4.60	4.54	6.36E-1	3.15E-1	1.81E-3

^a T = 25°C; I = 0.02; [Cl⁻] = 10⁻¹ M. From Lee, G.F., in *Principles and Applications of Water Chemistry*, S.D. Faust and J.V. Hunter (Eds.), John Wiley & Sons, New York, 1967.



pH effects

10

- Role of pH in reactant speciation
 - HOCl vs OCl⁻
 - Phenolic vs phenate
- Maximum at mid-pH
 - Between K_a 's for HOCl and phenolic

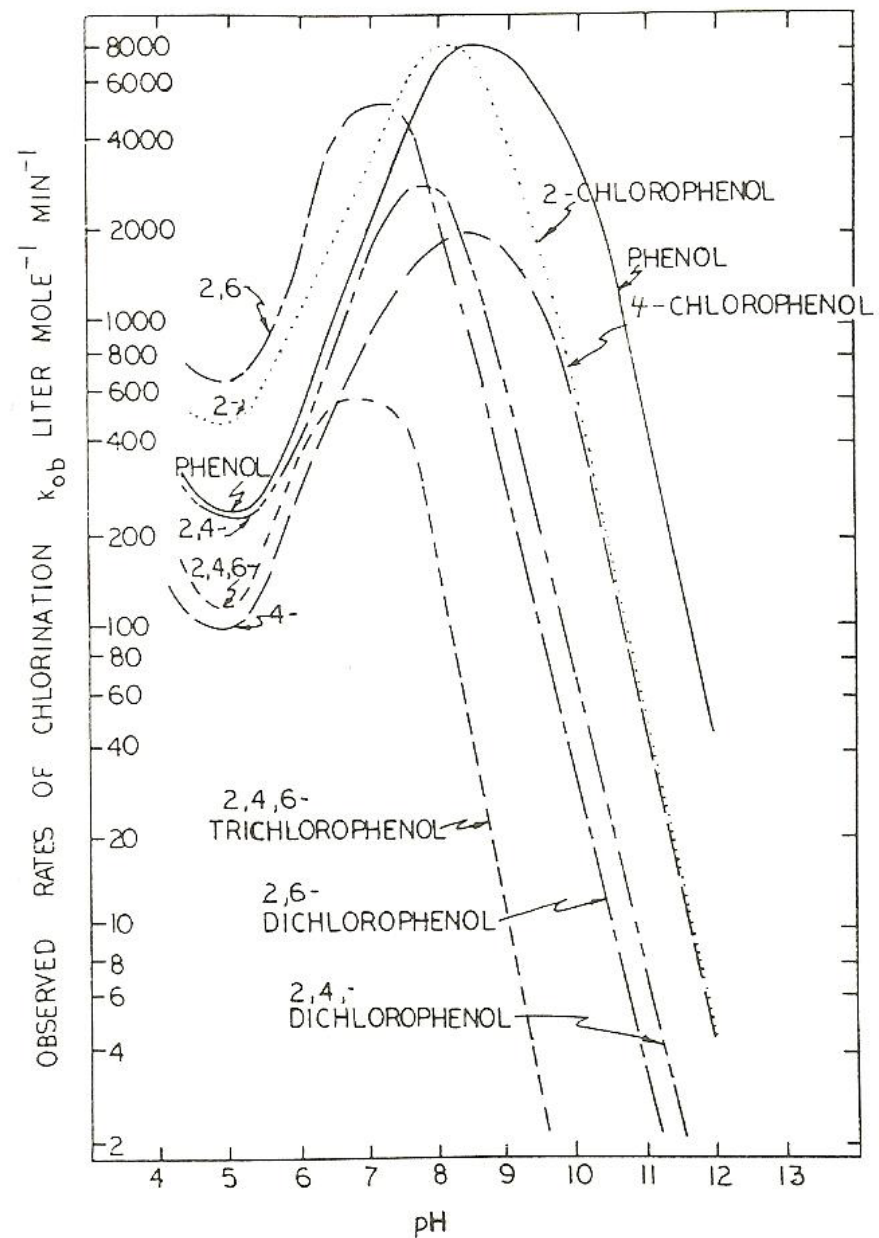
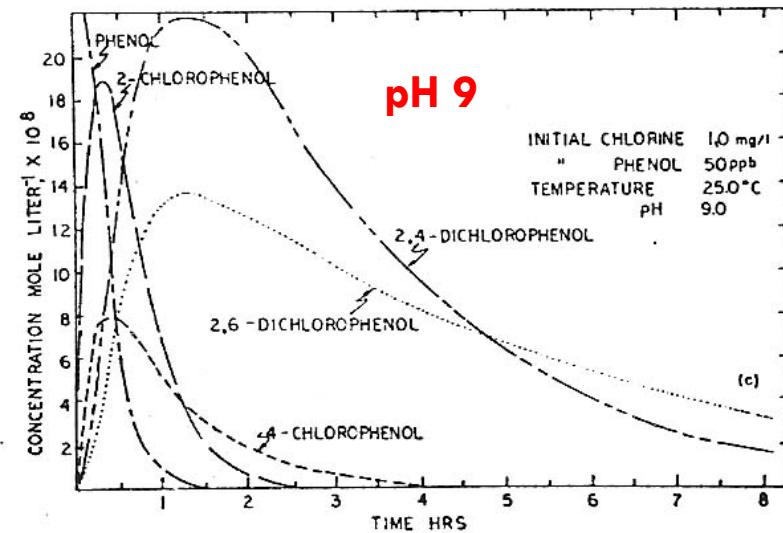
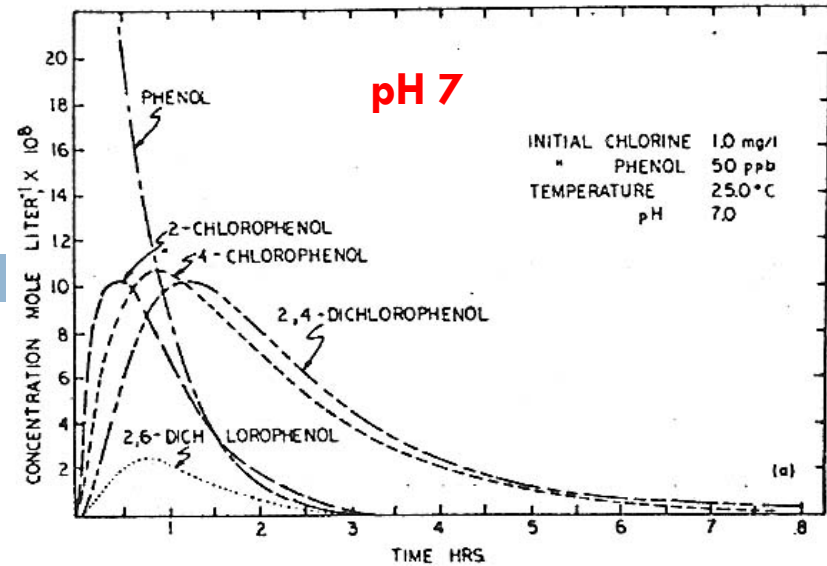
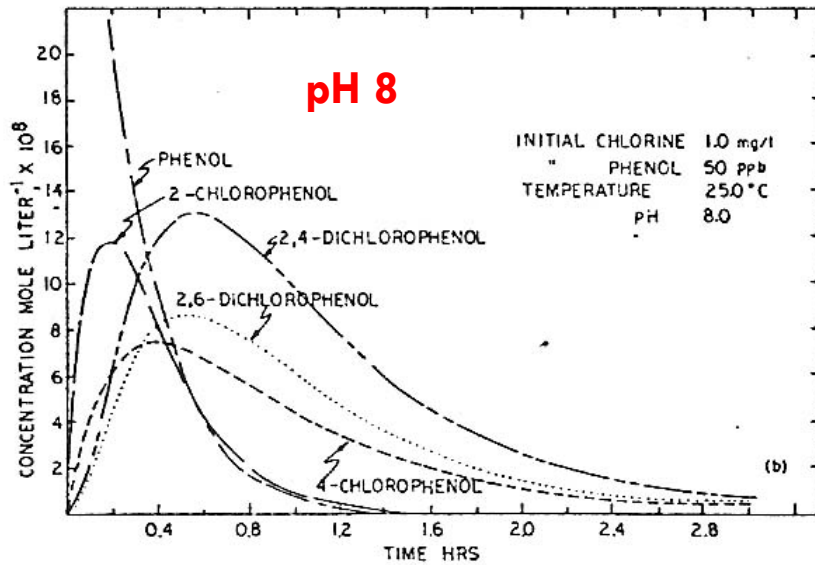


Figure 4-24. Variation in k_{obs} vs. pH for chlorination of phenol and various chlorophenol intermediates. [From Lee, G.F., in *Principles and Applications of Water Chemistry*, S.D. Faust and J.V. Hunter (Eds.), John Wiley & Sons, New York, 1967. With permission.]

Models I

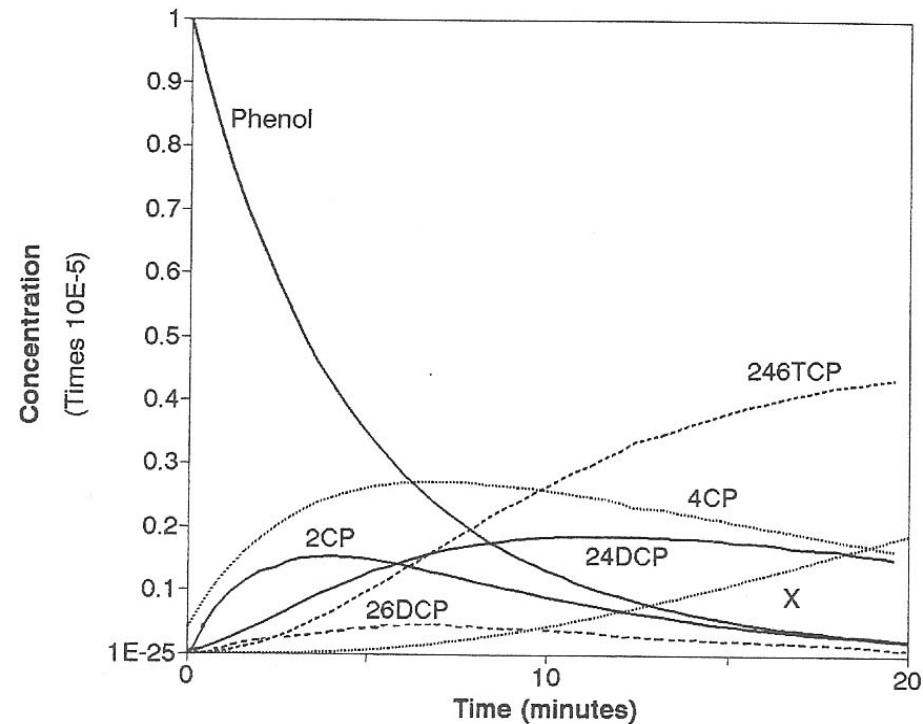
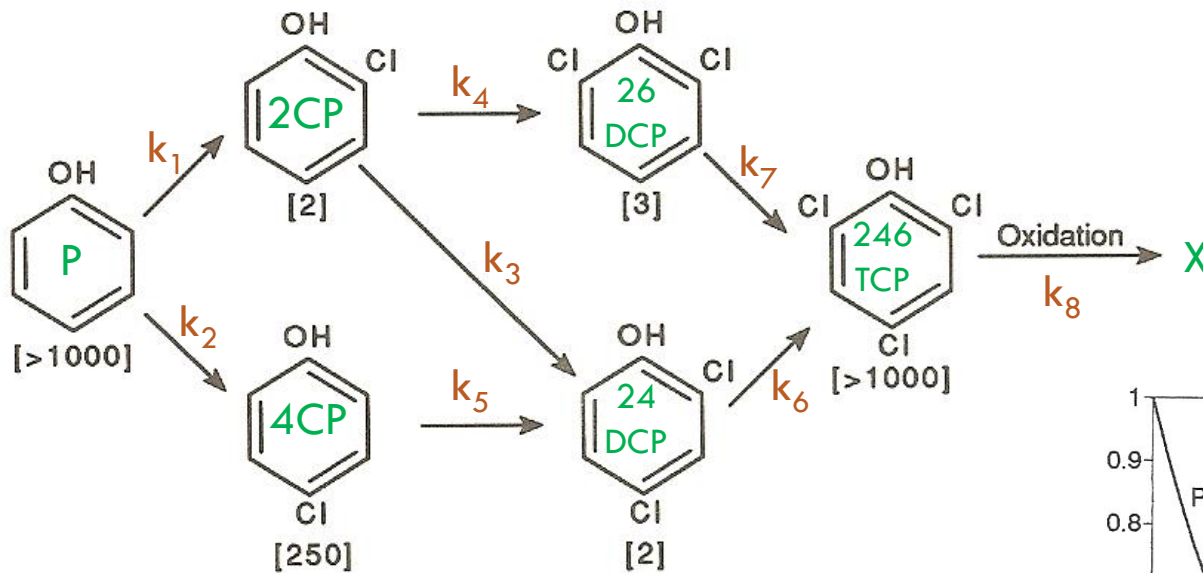
11

From: Lee, 1967



Modeling phenol chlorination II

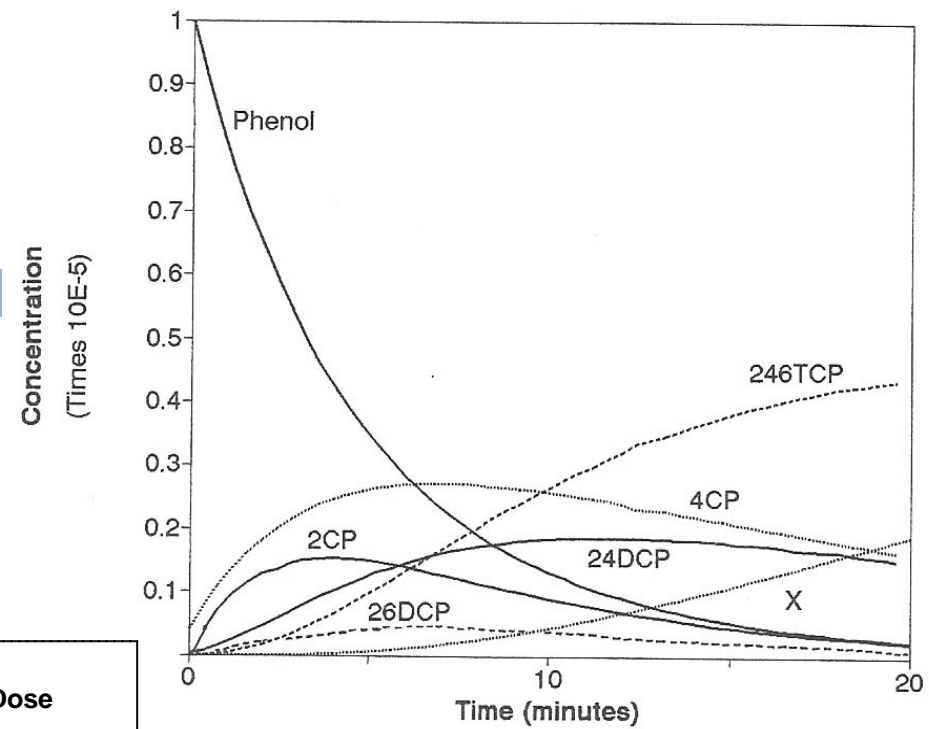
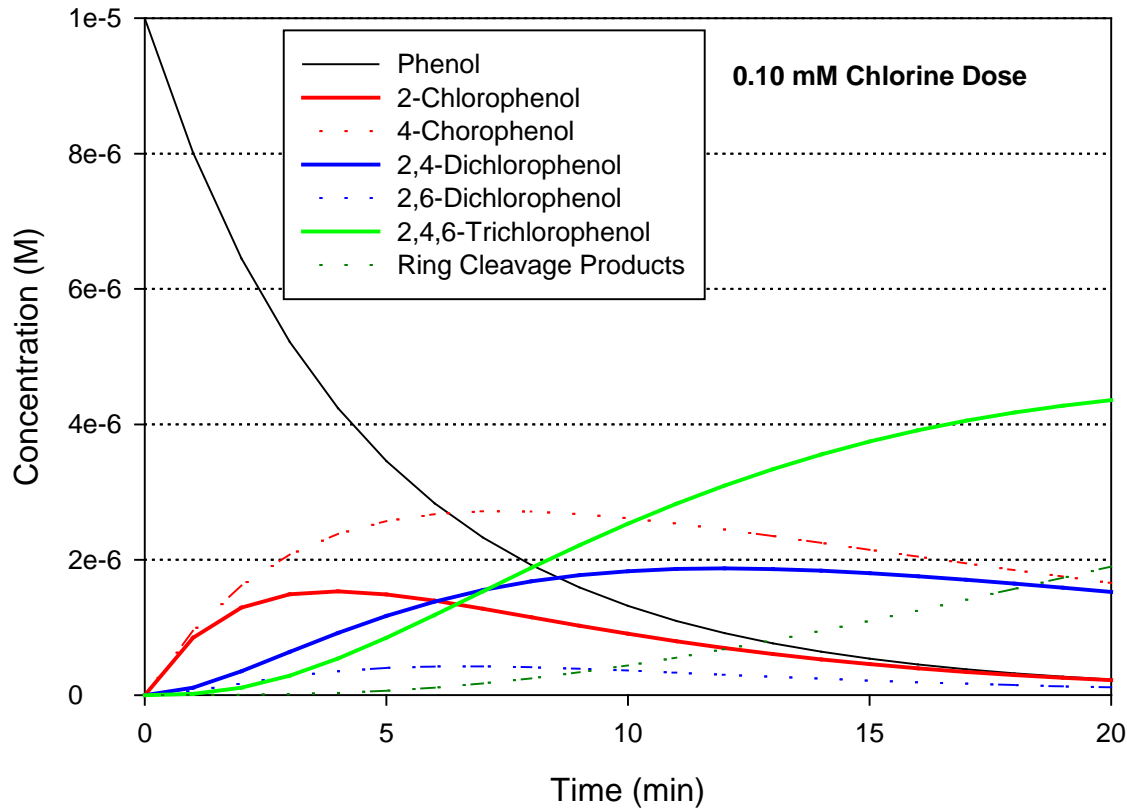
12



Models III

13

Scientist & Acuchem



- To next lecture