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CEE 690K
ENVIRONMENTAL REACTION KINETICS

Lecture #3

Rate Expressions: Sequential Reactions

Brezonik, pp.39-58, 240-241

David A. Reckhow

Introduction

Mechanisms: Haloform Reaction

- Chlorine + acetone
  - Morris & Baum, 1978
  - Brezonik, 1994 Pg 240-241

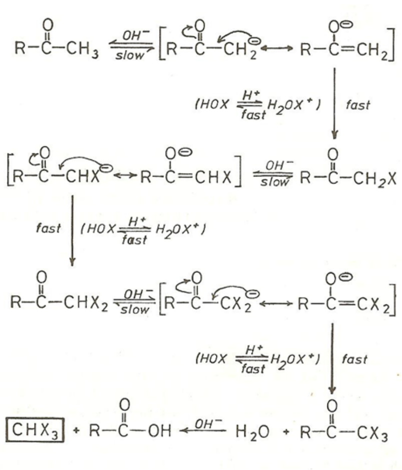

Figure 1. The reaction pathway of the haloform reaction.

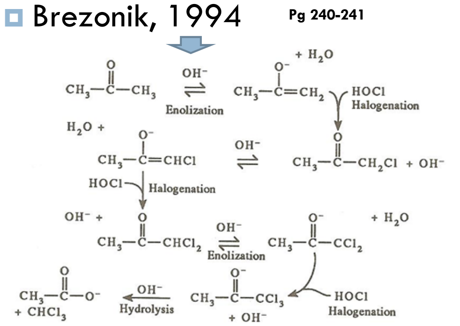

Figure 4-25. Reaction scheme for production of chloroform from acetone by the classic haloform reaction.

Haloform reaction: initial step

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- Three potential pathways to enolate
  - Reaction with water (K_O), hydroxide (K_{OH}), and proton (K_H)
    - $k_f = K_O + K_{OH}[OH^-] + K_H[H^+]$
    - 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	4.7×10^{-10}	0.25	2.9×10^{-5}	7500	385
Chloroacetone	16.5	5.3×10^{-8}	93	6.3×10^{-5}	21	1.0
as-Dichloroacetone	15	7.3×10^{-6}	450	1.1×10^{-5}	3.7	0.21
Pyruvic acid[6]		4.5×10^{-7}				
Ethyl pyruvate[6]	16	4.7×10^{-7}				
Acetylacetone	9.0	1.1×10^{-2}				
Ethyl acetoacetate	10.7	1.2×10^{-3}				
Malonic acid		1.7×10^{-1}				

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

What is k_r?

Reactions in Series

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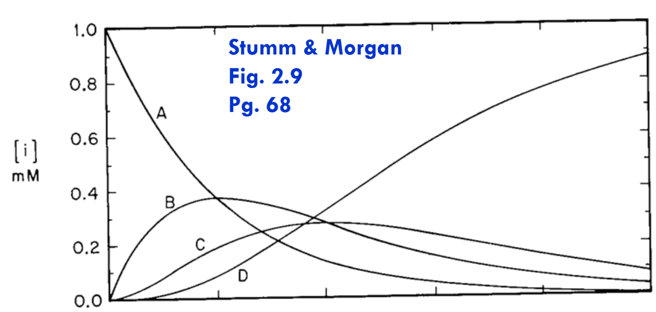
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

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



Consecutive Reactions I

$A \xrightarrow{k_i} B \xrightarrow{k_{ii}} C$

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- Overall rate determined by slowest step
  - If $k_i >> k_{ii}$
    - A rapidly forms B which then reacts slowly
    - $d[C]/dt \approx k_{ii}[B]$
  - If $k_i << k_{ii}$
    - 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

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Consecutive Reactions II

$A \xrightarrow{k_i} B \xrightarrow{k_{ii}} C$

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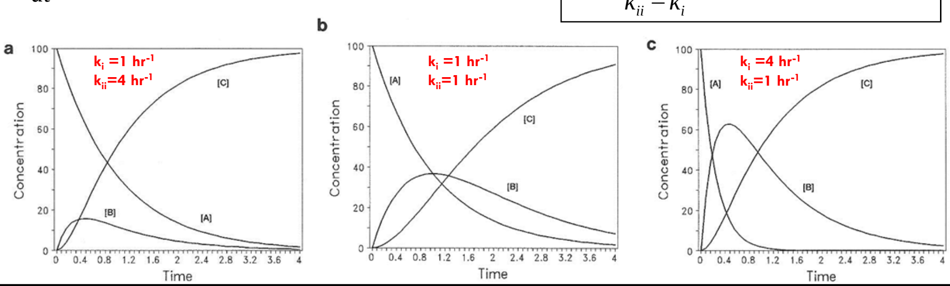
- Writing a separate equation for each species

$$\frac{d[A]}{dt} = -k_i[A] \Rightarrow [A] = [A]_0 e^{-k_i t}$$

$$\frac{d[B]}{dt} = k_i[A] - k_{ii}[B] \Rightarrow \frac{d[B]}{dt} = k_i\{[A]_0 e^{-k_i t}\} - k_{ii}[B] \Rightarrow [B] = \frac{k_i[A]_0}{k_{ii} - k_i}\{e^{-k_i t} - e^{-k_{ii} t}\}$$

$$\frac{d[C]}{dt} = k_{ii}[B] \Rightarrow [C] = \frac{[A]_0}{k_{ii} - k_i}\{k_{ii}(1 - e^{-k_i t}) - k_i(1 - e^{-k_{ii} t})\}$$

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



Limiting Cases

$$A \xrightarrow{k_i} B \xrightarrow{k_{ii}} C$$

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

- If $k_i >> k_{ii}$

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

- If $k_{ii} >> k_i$

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

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

If $k_i >> k_{ii}$:

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

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

If $k_{ii} >> k_i$:

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

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

Focusing on [B]

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- Often we are concerned with the maximum concentration of "B"
  - This occurs when d[B]/dt = 0

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

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

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

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

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

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

Chlorination of Phenol

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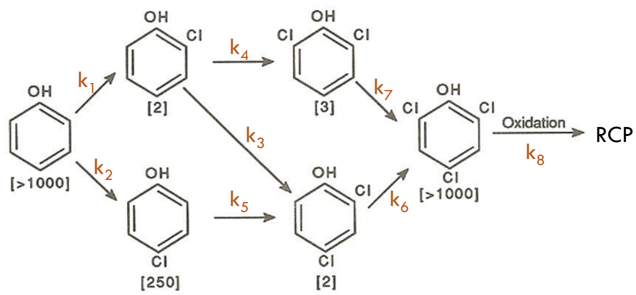
Table 4-8. Rate Constants (k_{obs}) for Chlorination of Phenols[a]

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

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

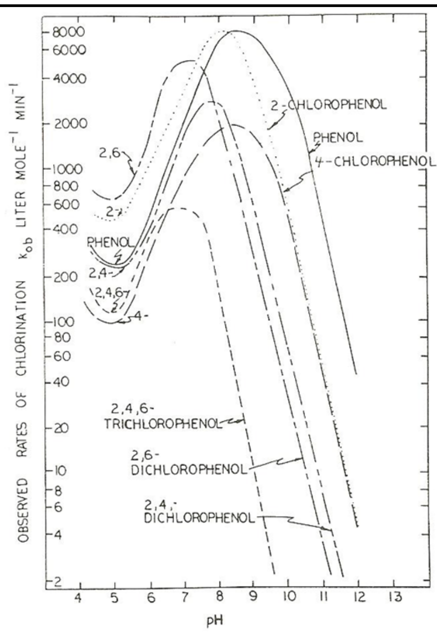

Figure 4-24. Variation in k_{obs} vs. pH for chlorination of phenol and various chlorophenol intermediates. [From Lee, G.F., in *Principles and Applications of Water Chemistry,* S.D. Faust and J.V. Hunter (Eds.), John Wiley & Sons, New York, 1967. With permission.]

Models I

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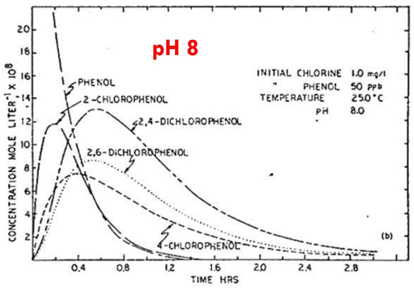
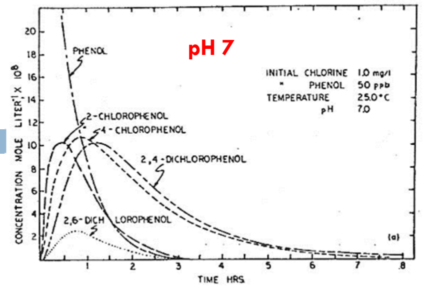
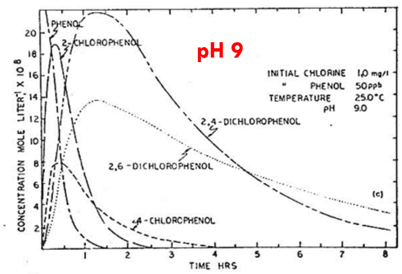
From: Lee, 1967







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Modeling phenol chlorination II

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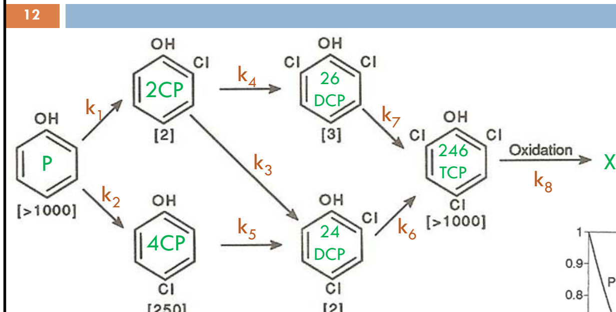

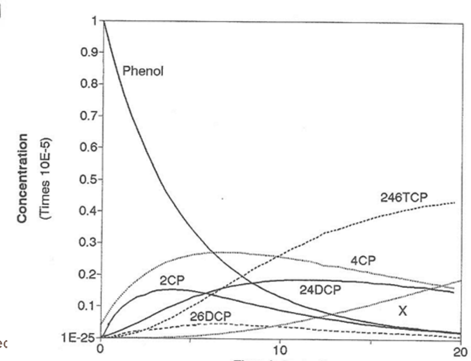

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Models III

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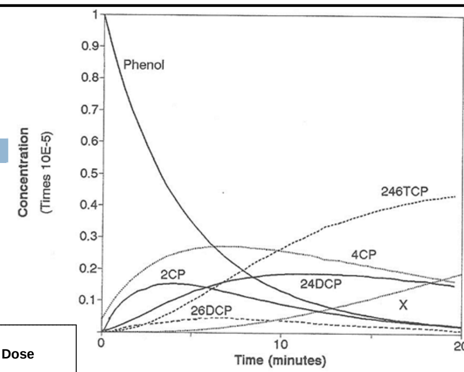
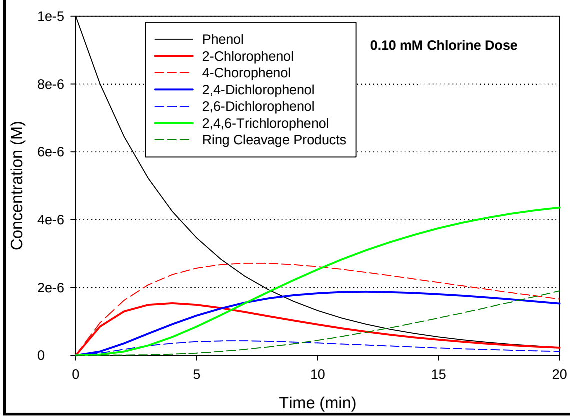
- Scientist & Acuchem





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- [To next lecture]()