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CEE 690K
ENVIRONMENTAL REACTION KINETICS

Lecture #9

Reaction Mechanisms: Acid Catalysis

Brezonik, Chapter 4

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Introduction

Mechanisms: Haloform Reaction

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

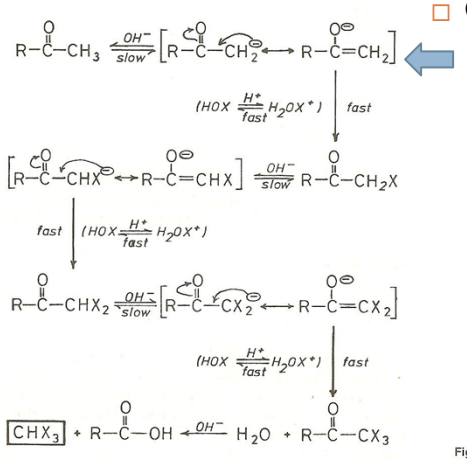

Figure 1. The reaction pathway of the haloform reaction.

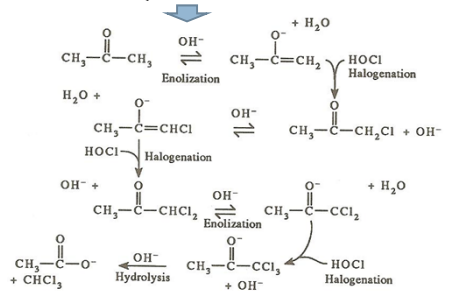

Figure 4-25. Reaction scheme for production of chloroform from acetone by the classic haloform reaction.

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?

Haloform: Doré's diagram

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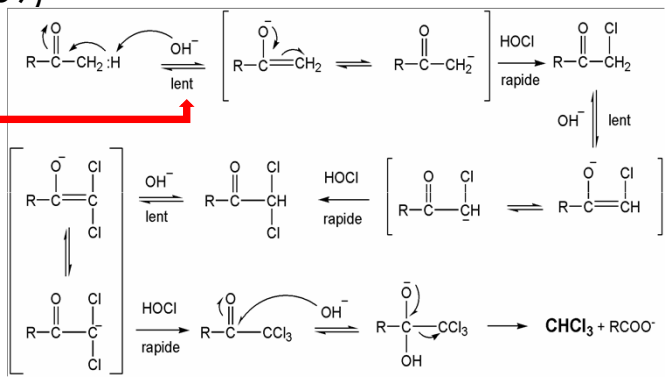
- Doré (1989)

RLS is the first one



Loss of intermediates in lab water

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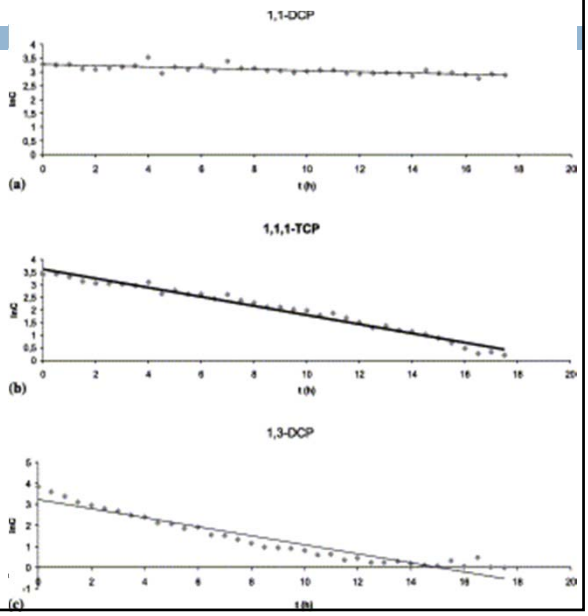
- 21C, ultrapure water
  - (Nikolaou et al., 2001)



Profile of TCP in water systems

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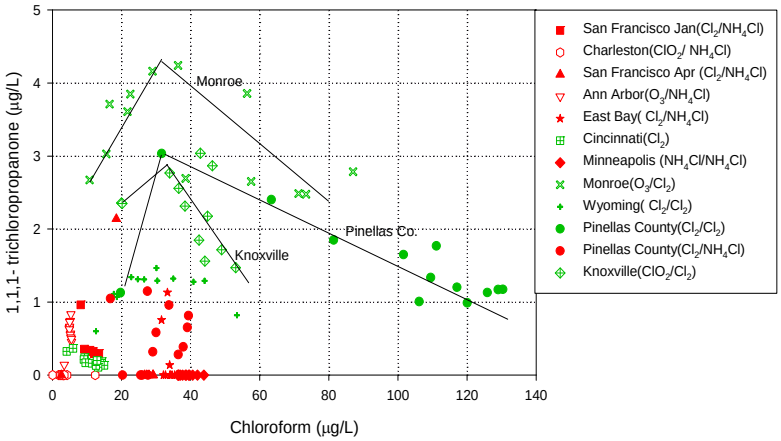
- **1,1,1-Trichloropropanone concentrations compared to the corresponding TTHM concentration for all samples**



Reckhow

Loss in water heaters

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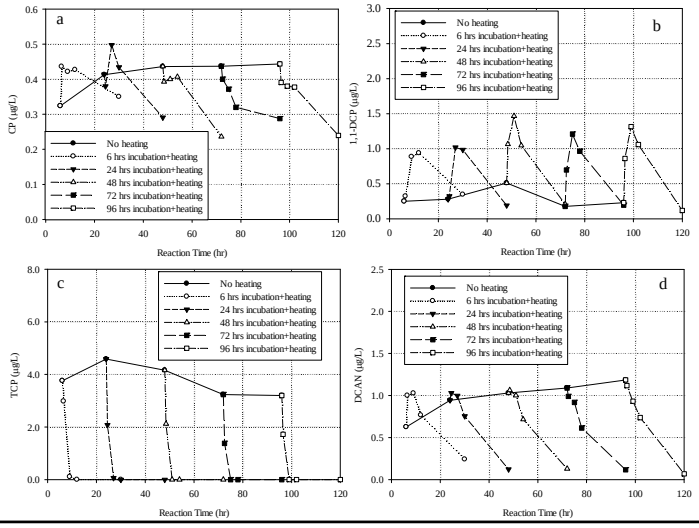
- Liu et al., 2013
  - In review



Case Study: TCP

Note: both TCP and TCAC refer to the 1,1,1-trichloropropanone

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- Observed loss of 1,1,1-trichloropropanone in distribution systems
  - Lab studies show that chloroform is the product
  - Logically presumed to be a simple hydrolysis

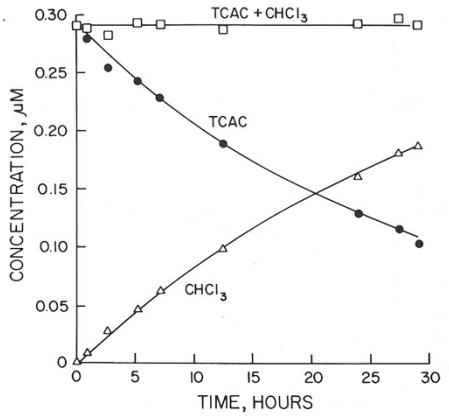

Figure 6. Chlorination of 1,1,1-trichloroacetone (TCAC). Conditions: 20.4 mg/L applied HOCl, $[PO_4]_T$ = 0.0145 *M*, pH 7.0, 20°C.

Reckhow & Singer, 1985
"Mechanisms of Organic Halide Formation During Fulvic Acid Chlorination and Implications with Respect to Preozonation", In Jolley et al., Water Chlorination; Chemistry, Environmental Impact and Health Effect, Volume 5, Lewis.

TCP (cont.)

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- Ionic strength effects

$$\ln k_H = -4.81 - 1.4\sqrt{I}$$

$$\log k_H = -2.08 - 0.6\sqrt{I}$$

- Rate with chlorine
  - Increases greatly
  - High intercept

$$k_T = 0.024 + 32[HOCl]_T$$

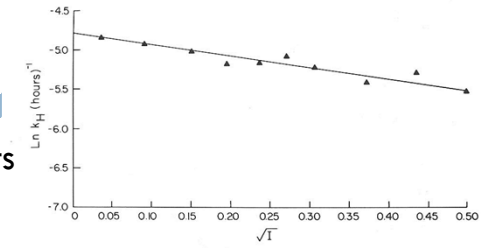

Figure 8. Pseudo first-order reaction rate constants for the hydrolysis of 1,1,1-trichloroacetone as a function of ionic strength. Conditions: pH 7.0, 20°C, no added chlorine.

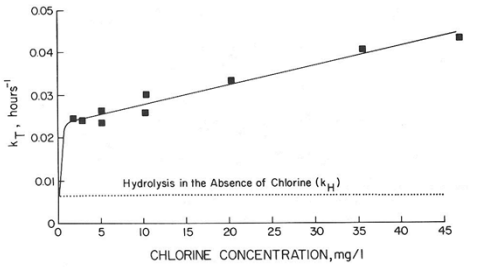

Figure 9. Pseudo first-order reaction rate constants for the disappearance of 1,1,1-trichloroacetone as a function of chlorine dose. Conditions: pH 7.0, 20°C, $[PO_4]_T$ = 0.0145 *M*.

Disagreement with prior study

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- Gurol & Suffet showed 10x higher rate constants
- Phosphate?

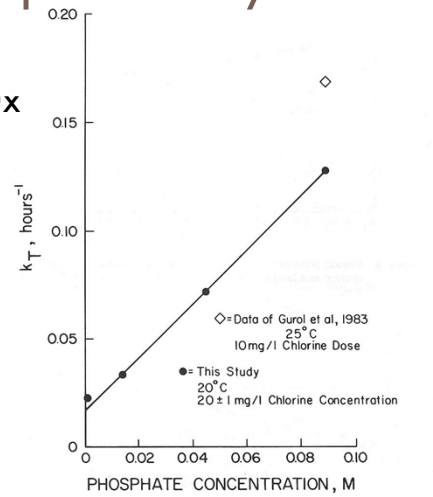

Figure 7. Pseudo first-order reaction rate constants for the chlorination of 1,1,1-trichloroacetone as a function of phosphate concentration at pH 7.0.

Putting it together

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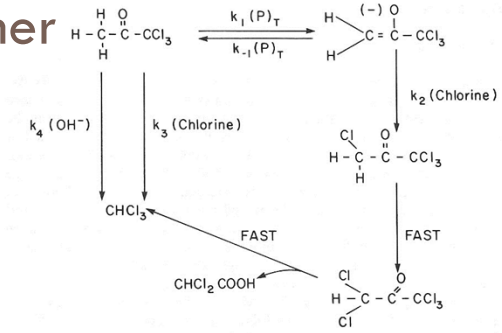

$$k_T = \frac{k_1 k_2 (\text{Chlorine}) (P)_T}{k_{-1} (P)_T + k_2 (\text{Chlorine})} + k_3 (\text{Chlorine}) + k_4 (OH^-)$$

where $k_1 = 1.25\ M^{-1}\ hr^{-1}$, $k_{-1} = 1.6 \times 10^{-7} / k_{TCAC}$, $k_3 = 32\ M^{-1}\ hr^{-1}$, $k_2 > 10^{-4} / k_{TCAC}$, $k_4 = 64{,}000\ M^{-1}\ hr^{-1}$

$$k_{TCAC} = \frac{(\text{Enolate}) (H^+)}{(\text{Keto-enol})}$$

Figure 12. Hypothetical mechanism for the decomposition of trichloroacetone to chloroform in the presence of intermediate concentrations of phosphate at pH 7.

Catalysis

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- Homogeneous Catalysis
  - Definition
    - Liquid-phase substances which react with the main reactants or intermediates thereby providing an alternative pathway to products with a lower activation energy or a higher frequency factor. Catalysts are often regenerated over the course of the reaction.

$$2A^{+2} + B^{+} \rightarrow 2A^{+} + B^{+3}$$

termolecular reaction? – be skeptical

What really happens:

$$A^{+2} + C^{+} \rightarrow A^{+} + C^{+2}$$
$$A^{+2} + C^{+2} \rightarrow A^{+} + C^{+3}$$
$$C^{+3} + B^{+} \rightarrow C^{+} + B^{+3}$$
$$2A^{+2} + B^{+} \rightarrow 2A^{+} + B^{+3}$$

"C" serves as a sort of charge-transfer facilitator, since "B" does not exist in a divalent state

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- Summary

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 $k_3 << k_2[A^-]$ 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 $k_3 >> k_2[A^-]$; 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 $k_3 << k_2[BH^+]$ regardless of nature of proton acceptor in first step.
V. General base	$HS + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S^- + BH^+$ $S^- + H_2O \xrightarrow[\text{fast}]{k_3} P + OH^-$	$P = k[HS][B]$ $P = [HS]\{\Sigma k[B]\}$	Expression applies when $k_3 >> k_2[BH^+]$; 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.

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- To next lecture