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CEE 690K

ENVIRONMENTAL REACTION KINETICS

Lecture #9

Reaction Mechanisms: Acid Catalysis

Brezonik, Chapter 4

Mechanisms: Haloform Reaction

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□ Chlorine + acetone

□ Morris & Baum, 1978

□ Brezonik, 1994

Pg 240-241

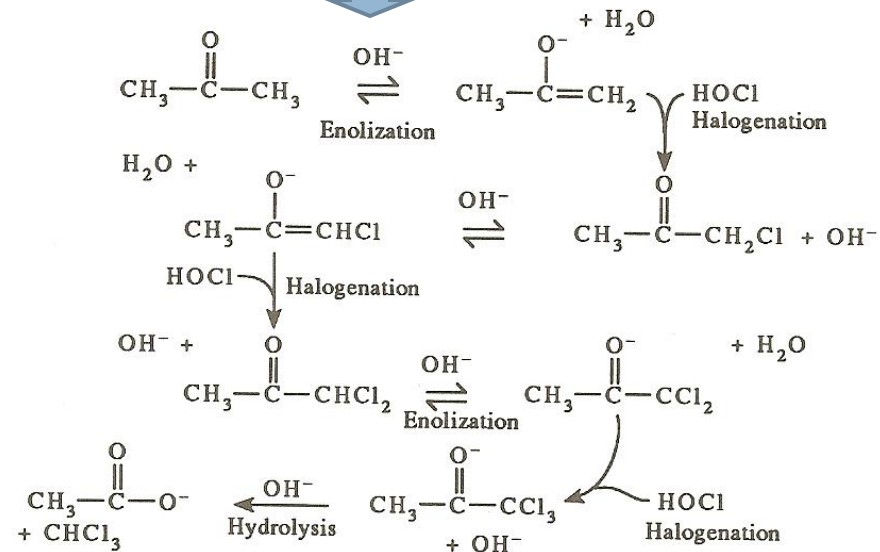
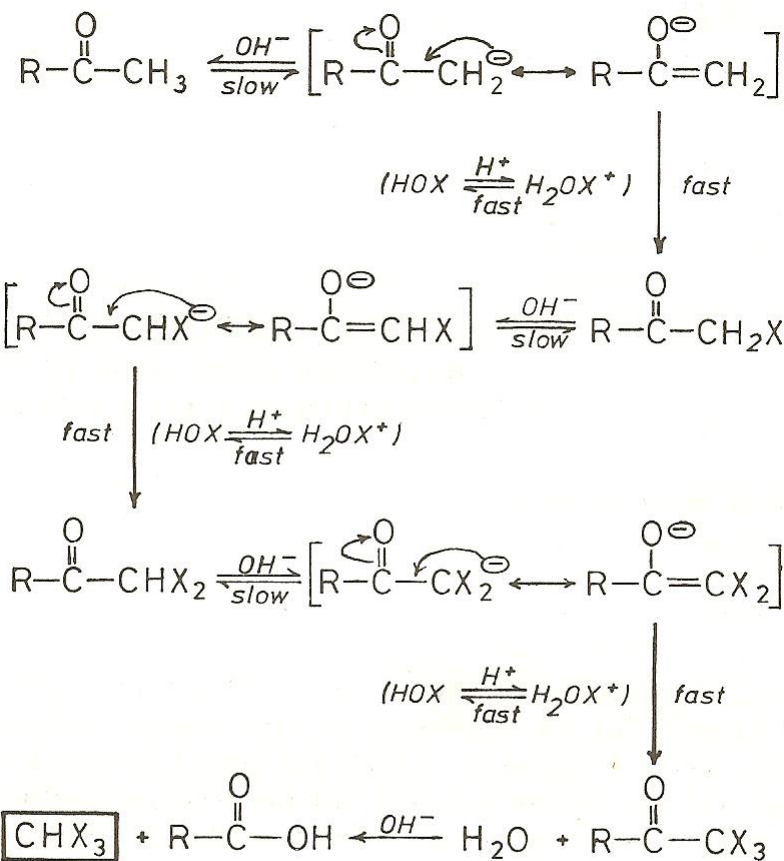


Figure 4-25. Reaction scheme for production of chloroform from acetone by the classic haloform reaction.

Halof orm reaction: initial step

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- Three potential pathways to enolate
 - Reaction with water (K_O), hydroxide (K_{OH}), and proton (K_H)
 - $k_f = K_O + K_{OH}[\text{OH}^-] + K_H[\text{H}^+]$
 - 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				

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

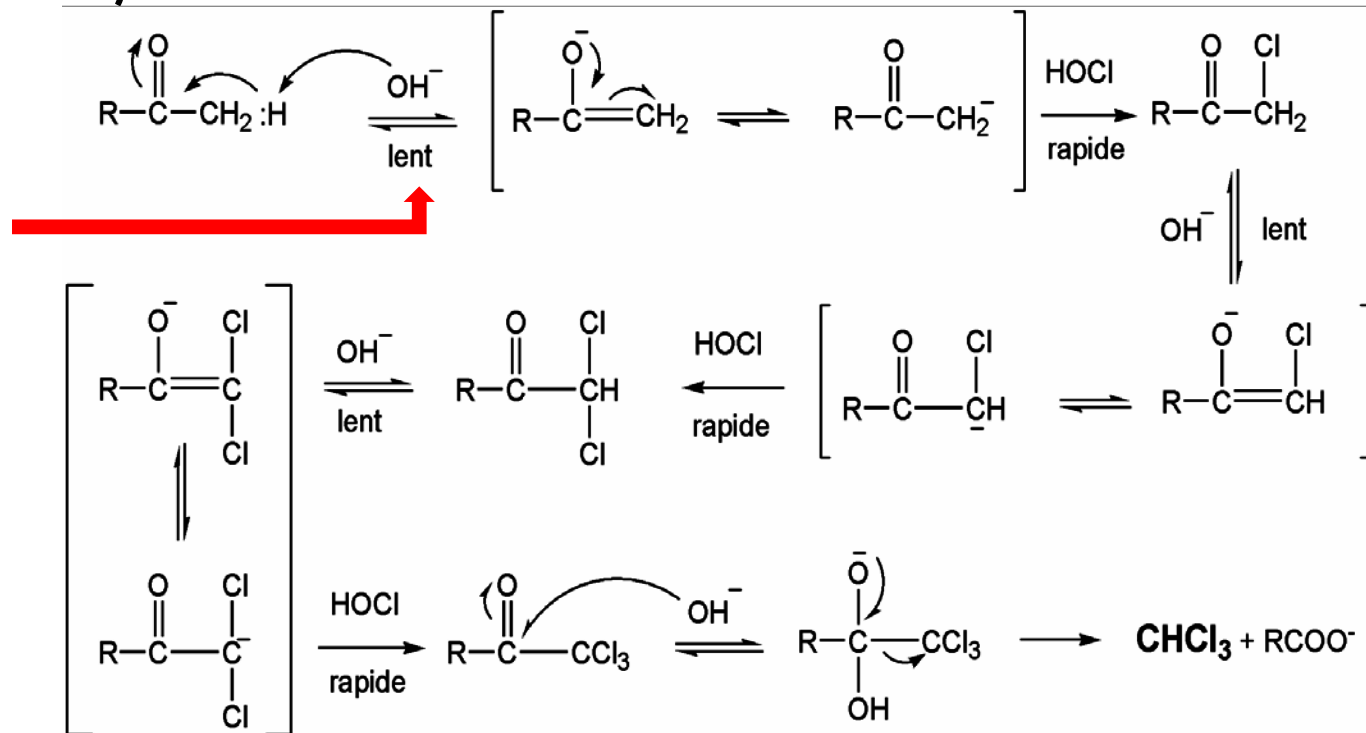
What is k_r ?

Haloform: Doré's diagram

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□ Doré (1989)

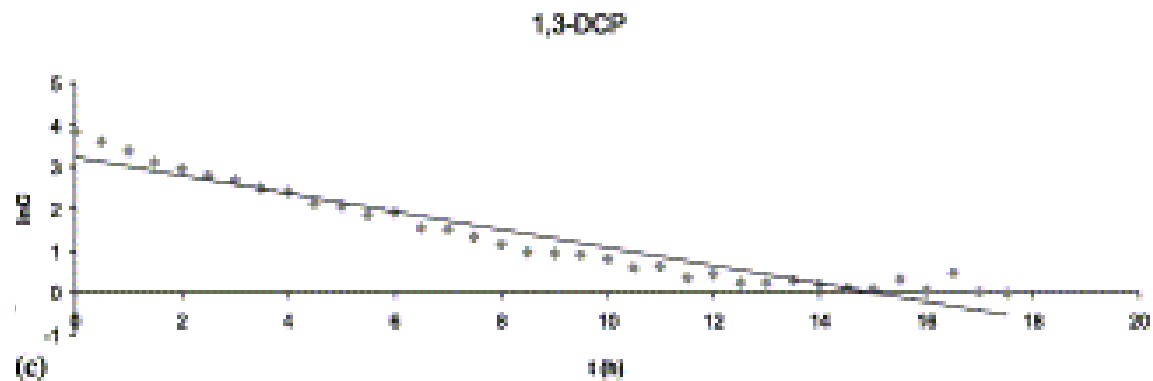
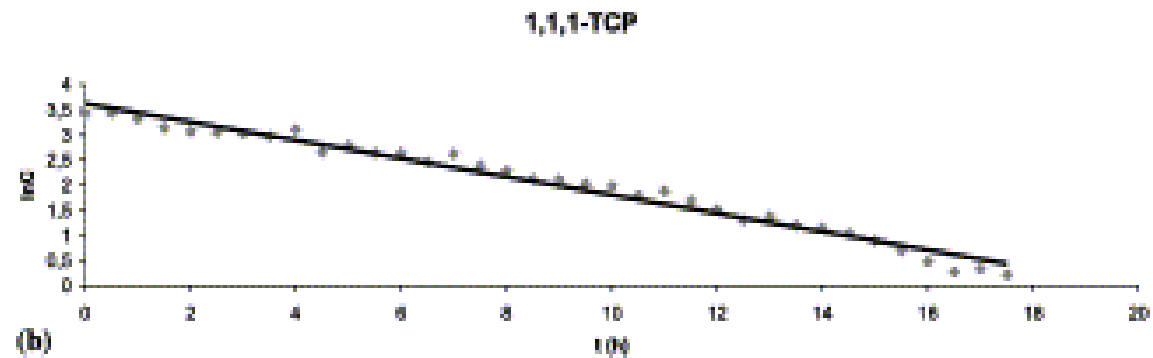
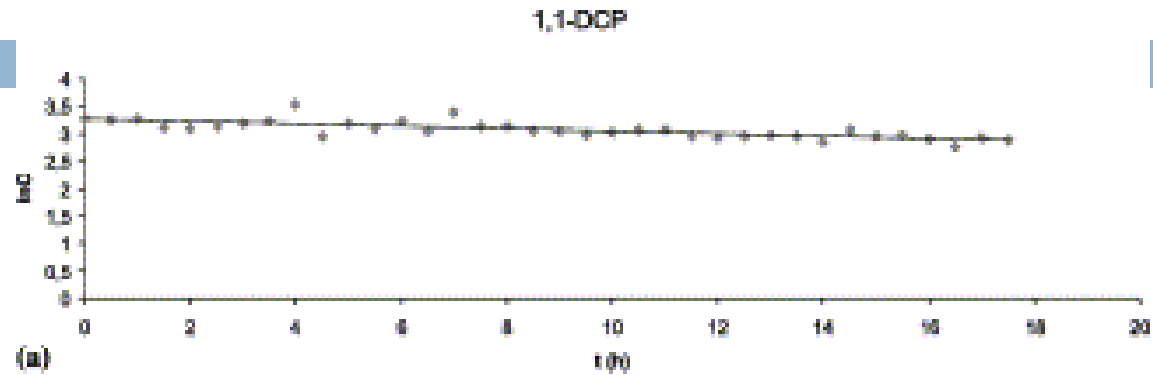
RLS is the first one



Loss of intermediates in lab water

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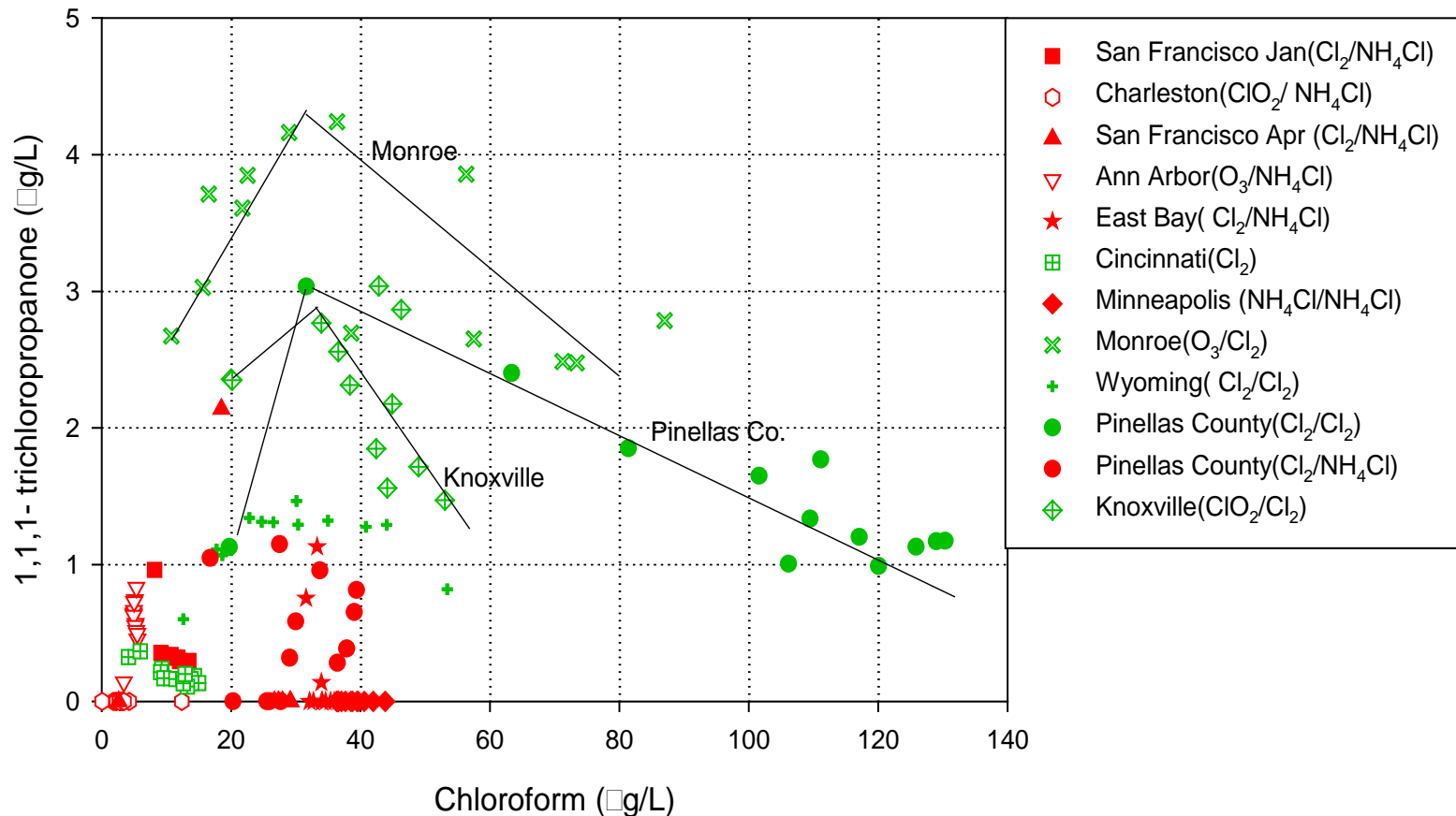
- 21°C, ultrapure water
- (Nikolaou et al., 2001)



Profile of TCP in water systems

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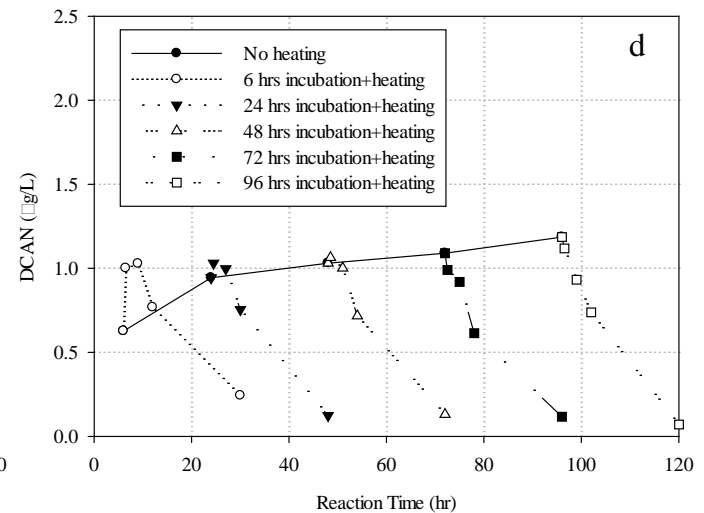
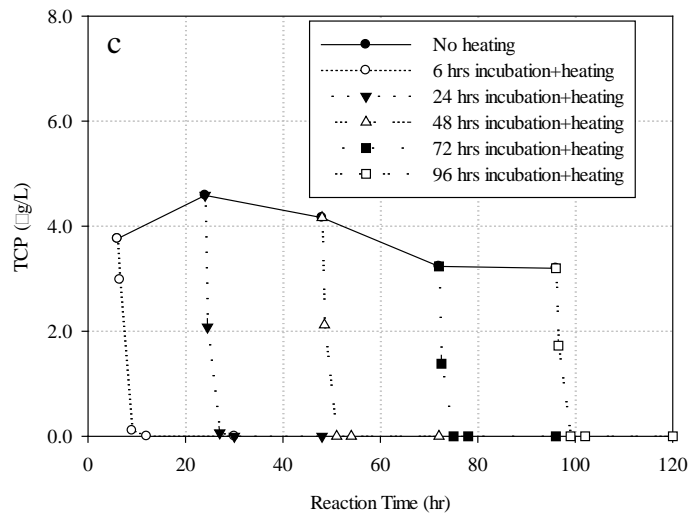
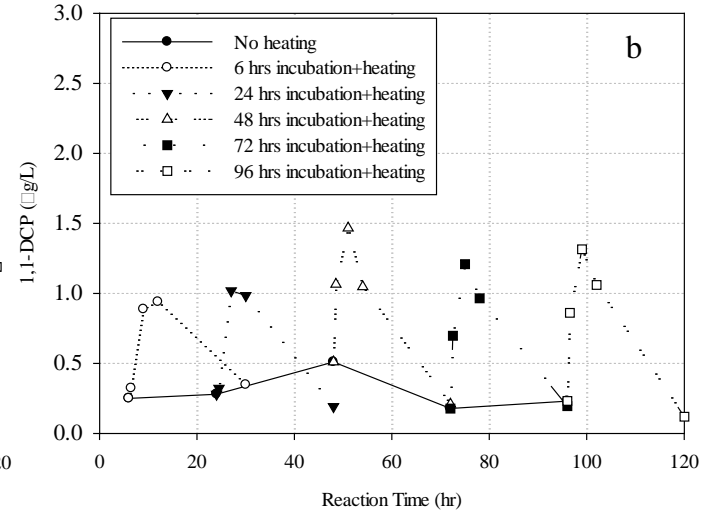
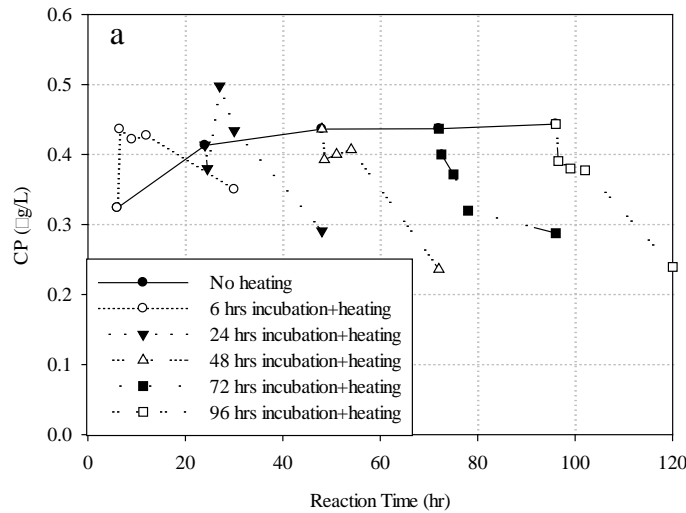
- 1,1,1-Trichloropropanone concentrations compared to the corresponding TTHM concentration for all samples



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

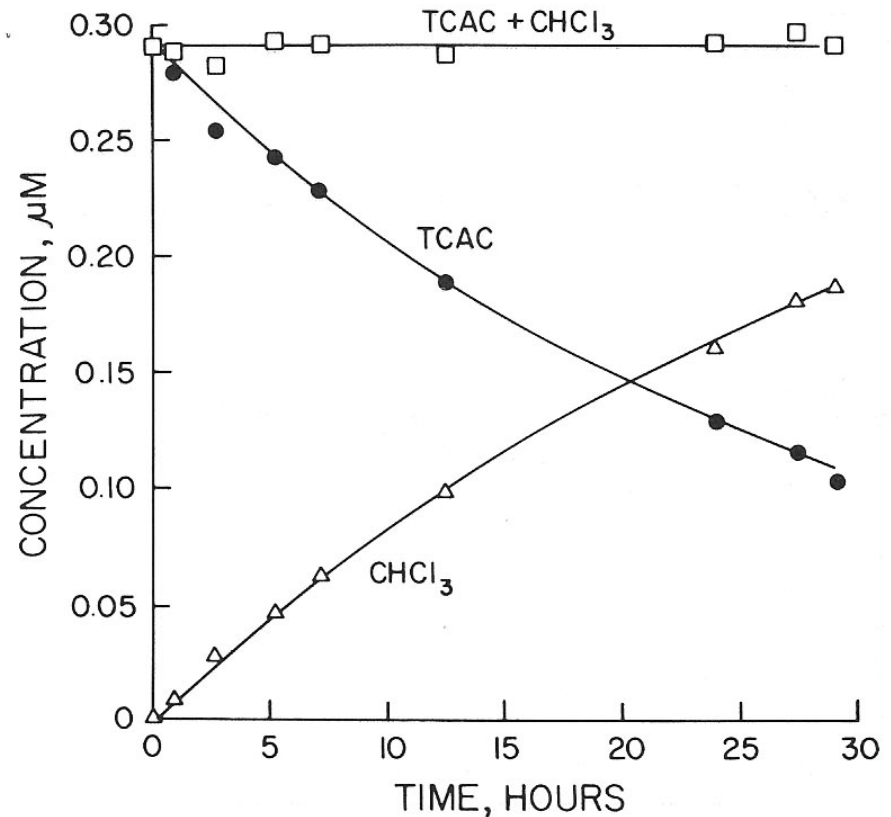


Figure 6. Chlorination of 1,1,1-trichloroacetone (TCAC). Conditions: 20.4 mg/L applied HOCl, $[PO_4]_T = 0.0145 M$, pH 7.0, 20°C.

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

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

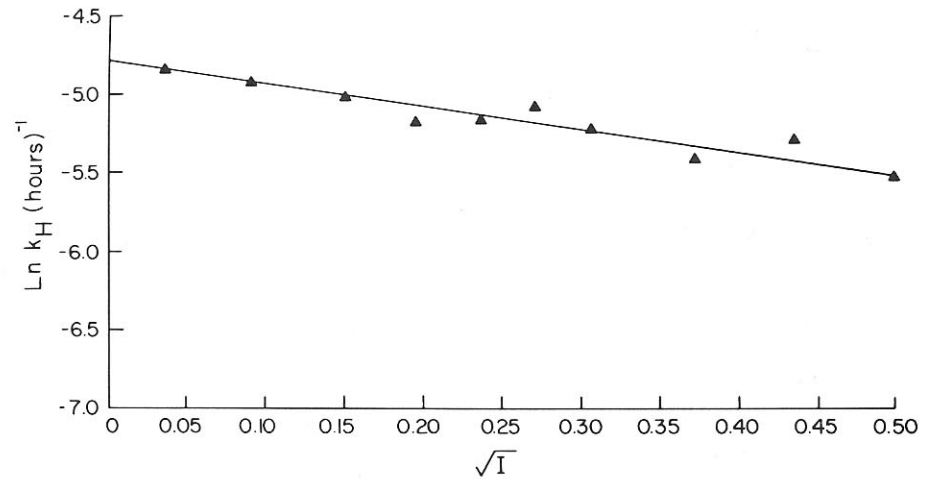


Figure 8. Pseudo first-order reaction rate constants for the hydrolysis of 1,1,1-trichloroacetone as a function of ionic strength. Conditions: pH 7.0, 20°C, no added chlorine.

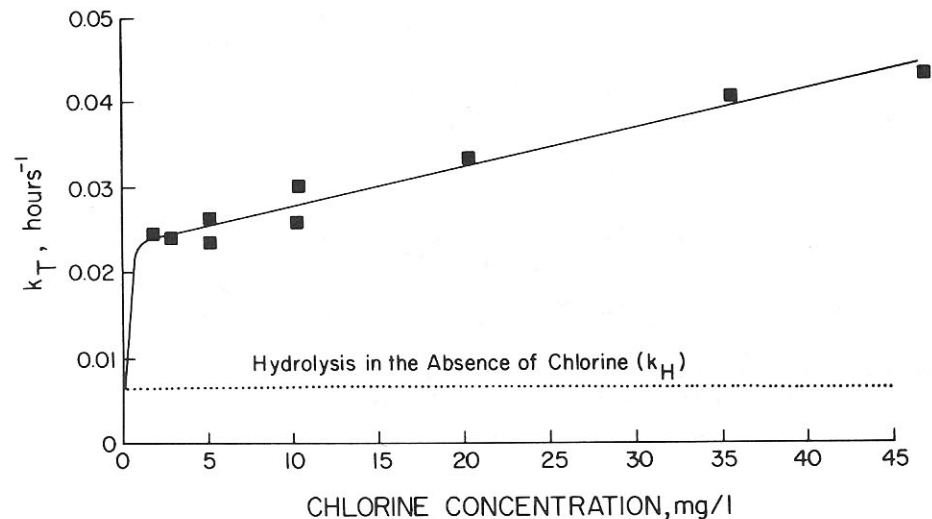


Figure 9. Pseudo first-order reaction rate constants for the disappearance of 1,1,1-trichloroacetone as a function of chlorine dose. Conditions: pH 7.0, 20°C, $[PO_4]_T = 0.0145$ M.

Disagreement with prior study

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

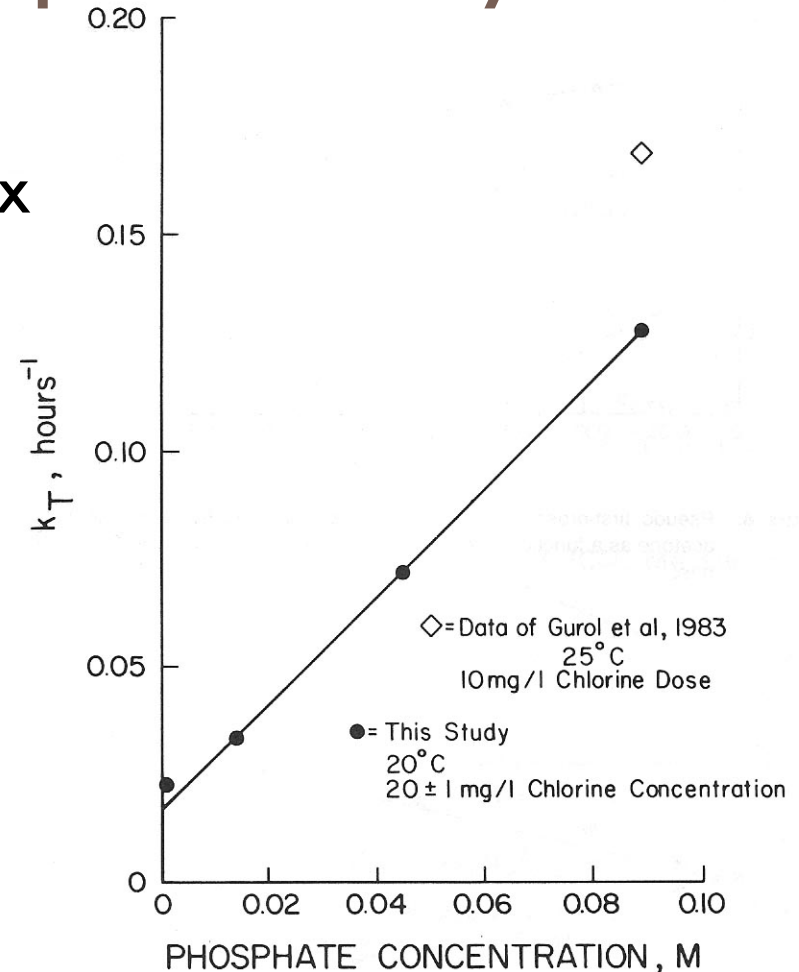
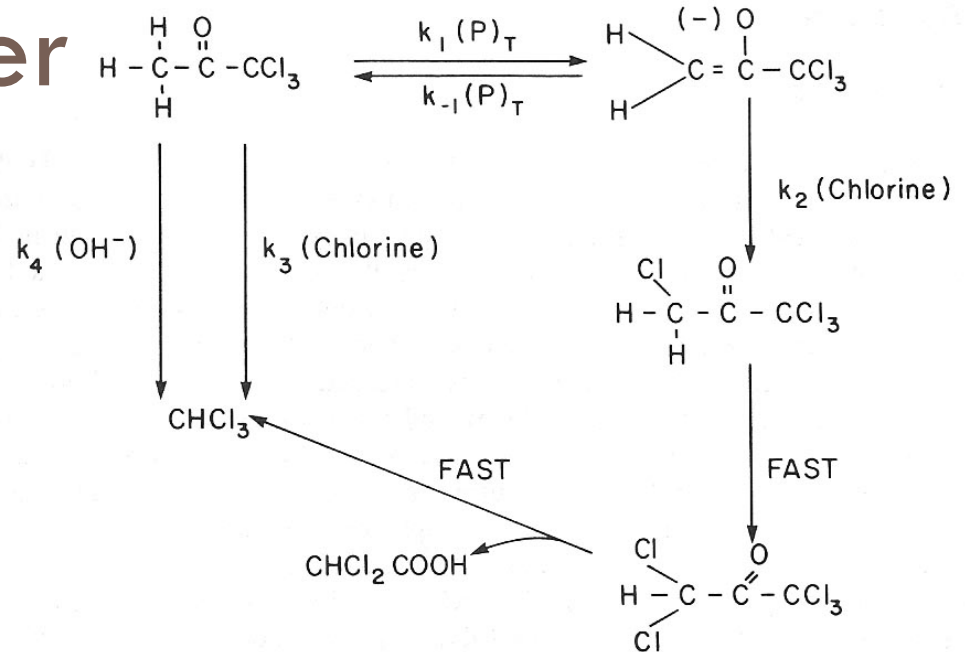


Figure 7. Pseudo first-order reaction rate constants for the chlorination of 1,1,1-trichloroacetone as a function of phosphate concentration at pH 7.0.

Putting it together

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

where

$$k_1 = 1.25 \text{ M}^{-1} \text{ hr}^{-1}$$

$$k_3 = 32 \text{ M}^{-1} \text{ hr}^{-1}$$

$$k_4 = 64,000 \text{ M}^{-1} \text{ hr}^{-1}$$

$$k_{-1} = 1.6 \times 10^{-7} / k_{\text{TCAC}}$$

$$k_2 > 10^{-4} / k_{\text{TCAC}}$$

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

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

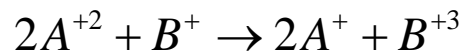
Catalysis

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□ Homogeneous Catalysis

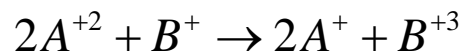
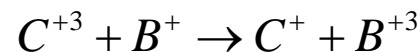
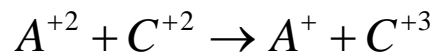
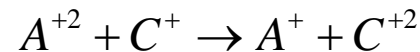
□ Definition

- 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.



termolecular reaction? – be skeptical

What
really
happens:



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

□ Summary

Table 4-1. Mechanisms of Acid-Base Catalysis

Type	Mechanism	Rate expression	Comments
I. Specific H ⁺	$S + HA \xrightleftharpoons[k_2]{k_1} SH^+ + A^-$ $SH^+ + H_2O \xrightarrow[\text{slow}]{k_3} P + H_3O^+$	$P = k_1 k_3 [S][HA] / k_2 [A^-]$ $= (k_1 k_3 / k_2 K_a) [S][H^+]$ 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 ₃ O ⁺ .
II. General acid	$S + HA \xrightleftharpoons[k_2]{k_1} SH^+ + A^-$ $SH^+ + H_2O \xrightarrow[\text{fast}]{k_3} P + H_3O^+$	$P = [S] \{ \sum k_i [HA] \}$	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	$S + HA \xrightleftharpoons[k_2]{k_1} SH^+ + A^-$ $SH^+ + A^- \xrightarrow{k_3} P + HA$	$P = \frac{k_1 k_3 [S][HA]}{(k_2 + k_3)}$ or $P = k' [S][HA]$	Prototropic mechanism yields general acid catalysis regardless of relative sizes of k_2 and k_3 .
IV. Specific OH ⁻	$HS + B \xrightleftharpoons[k_2]{k_1} S^- + BH^+$ $S^- + H_2O \xrightarrow[\text{slow}]{k_3} P + OH^-$	$P = k_1 k_3 [S^-][B] / k_2 [BH^+]$ $= (k_1 k_3 / k_2 K_B) [S^-][OH^-]$	For protolytic case, expression applies when $k_3 \ll k_2 [BH^+]$ regardless of nature of proton acceptor in first step.
V. General base	$HS + B \xrightleftharpoons[k_2]{k_1} S^- + BH^+$ $S^- + H_2O \xrightarrow[\text{fast}]{k_3} P + OH^-$	$P = k [HS][B]$ $P = [HS] \{ \sum k_i [B] \}$	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	$HS + B \xrightleftharpoons[k_2]{k_1} S^- + BH^+$ $S^- + BH^+ \xrightarrow{k_3} P + B$	$P = \frac{k_1 k_3 [S][HA]}{(k_2 + k_3)}$ or $P = k' [S][HA]$	Prototropic case yields general base catalysis regardless of relative sizes of k_2 and k_3 .

- To next lecture