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CEE697K Lecture #10 1

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CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #10

Special Topics: DCP in Water
Primary Literature (e.g., Guthrie & Cossar, 1986)

David A. Reckhow

Introduction

Guthrie

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- J. Peter Guthrie
  - Department of Chemistry Western University, London, Ontario, Canada, N6A 5B7

Western Science

Guthrie, J. P. and J. Cossar (1986). "The Chlorination of Acetone - A Complete Kinetic Analysis." Canadian Journal of Chemistry-Revue Canadienne De Chimie **64(6): 1250-1266.**

- B.Sc.
  - Univ. Western Ontario
- PhD Chemistry, 1968
  - Harvard University
  - DECARBOXYLATION AND ENAMINE FORMATION: MODEL SYSTEMS FOR ACETOACETATE DECARBOXYLASE
    - By James Peter Guthrie
- Princeton Univ.
- 1970, Faculty, Western University

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Mechanisms: Haloform Reaction

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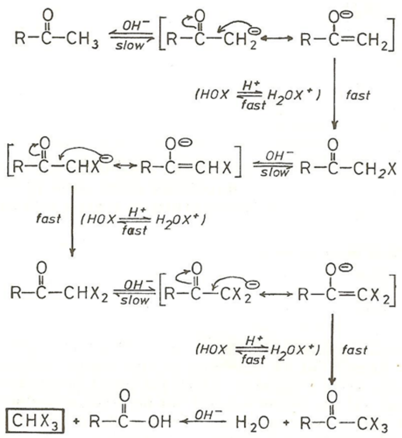

Figure 1. The reaction pathway of the haloform reaction.

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

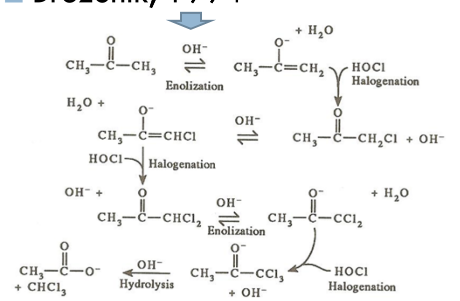

Figure 4-25. Reaction scheme for production of chloroform from acetone by the classic haloform reaction.

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} l/mol, sec	K_H l/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?

Guthrie & Cossar Pathway

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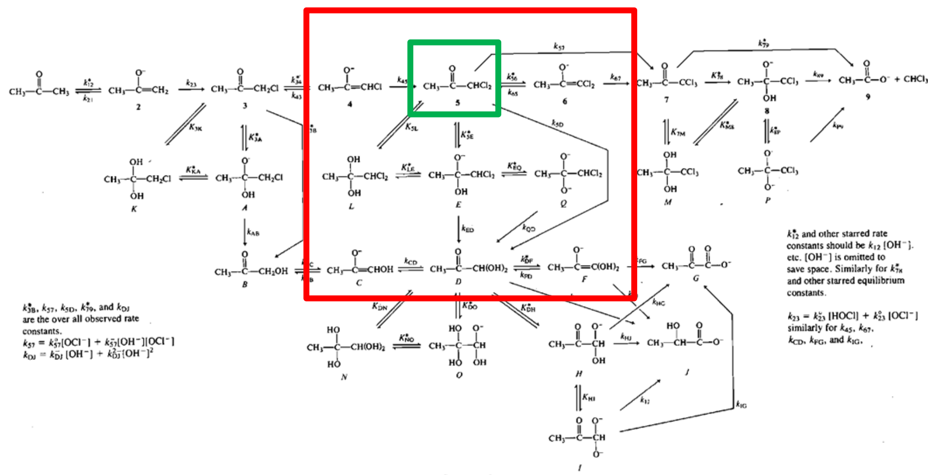
- Scheme 1



Scheme 1.

Hydrolysis of 1,1-DCP

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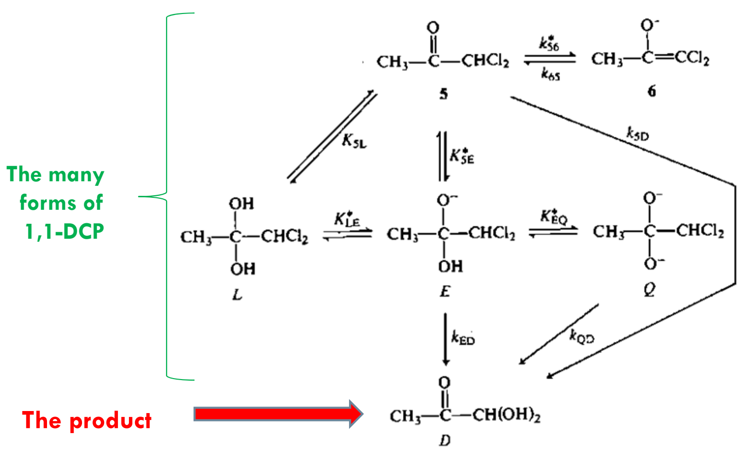
- a



DCP equilibria I

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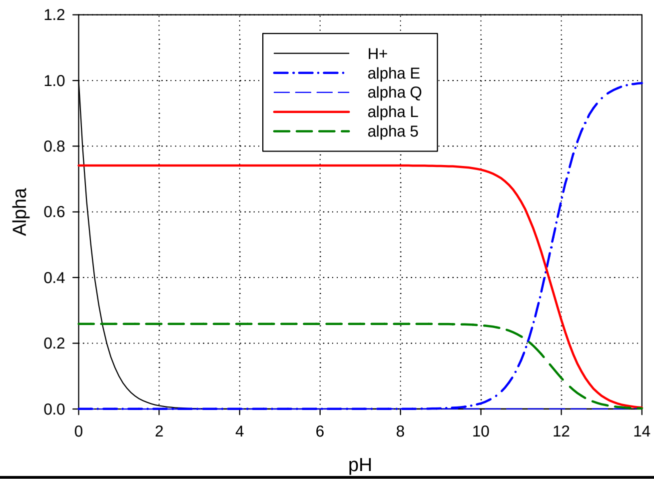
- Bell K's



DCP equilibria II

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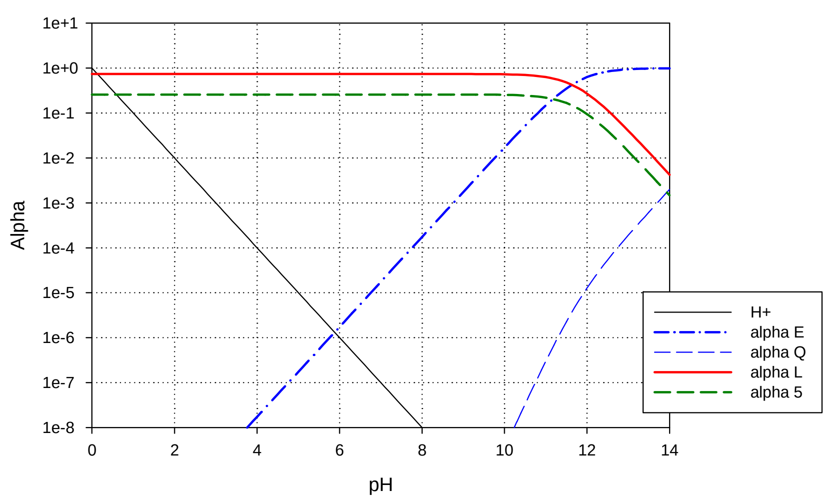
- Bell K's



DCP equilibria III

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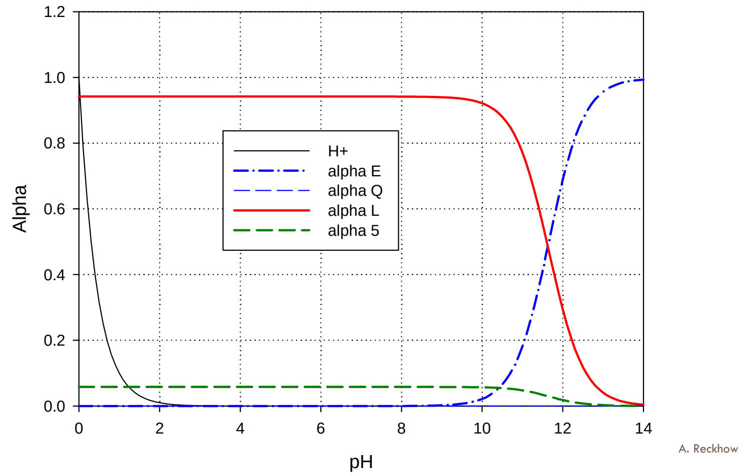
- Guthrie K's



DCP equilibria IV

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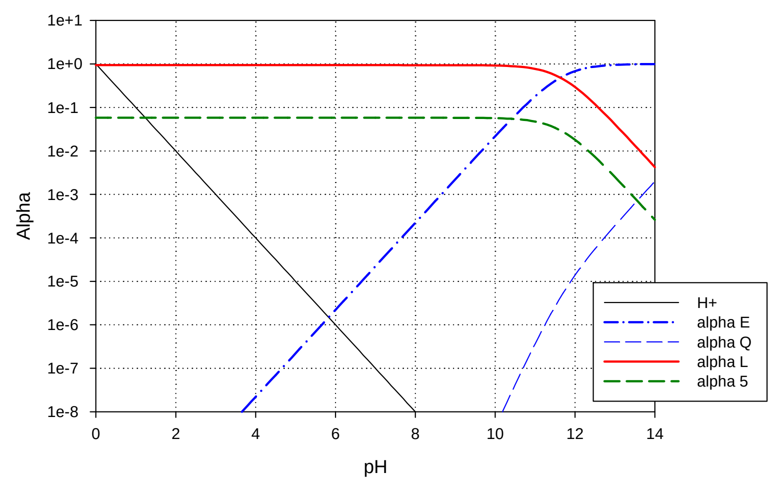
- Guthrie K's



Loss of intermediates in lab water

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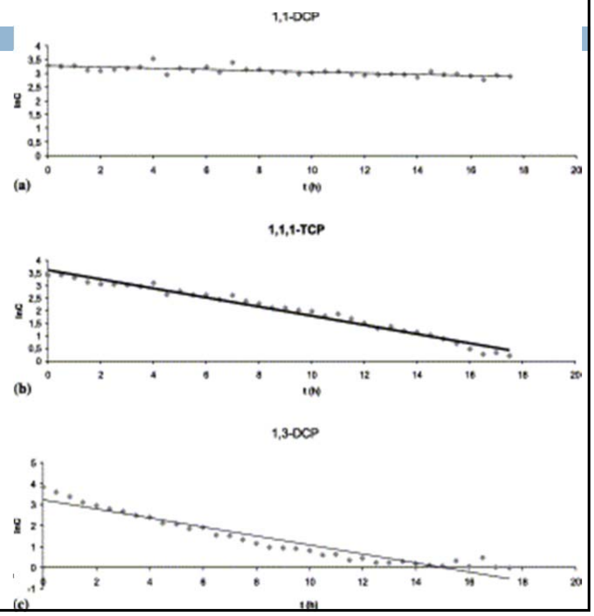
- 21C, ultrapure water
  - (Nikolaou et al., 2001)



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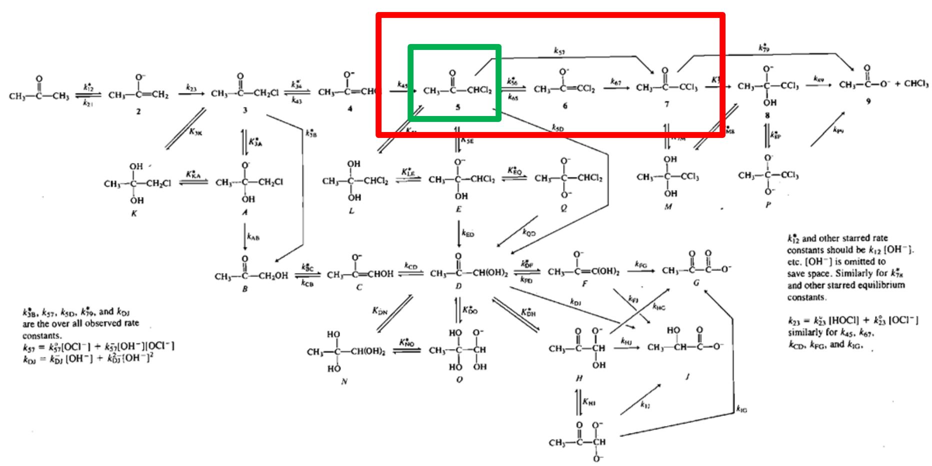
- chlorine



SCHEME 1.

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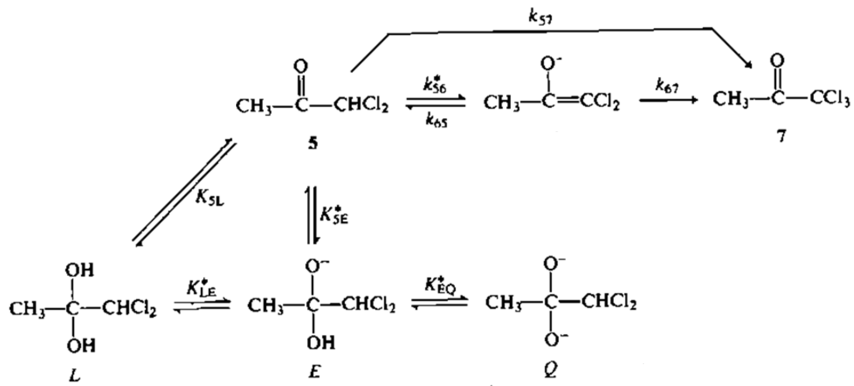
- a



Model

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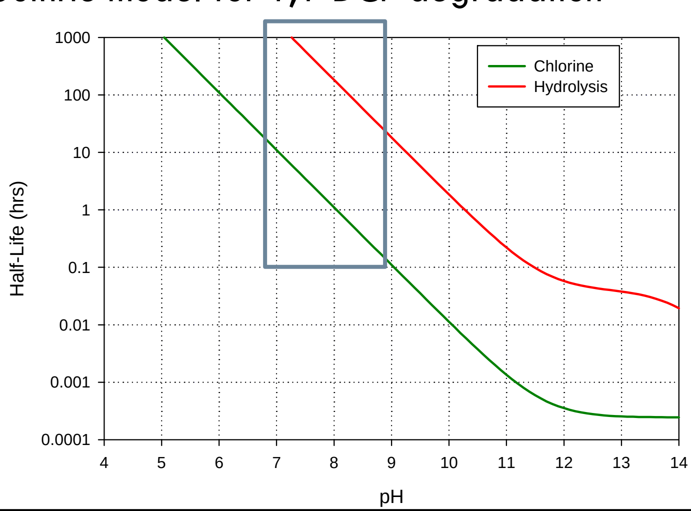
- Guthrie model for 1,1-DCP degradation



LFER Analysis

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- Baiyang Chen analysis
  - pH 7-7.5
  - 20-25C
- Predicted hydrolysis rate constant for 1,1-DCP is $10^{-1.66}$ hr^{-1}
  - Half-life of 31.7 hr
  - 6.1×10^{-6} sec^{-1}
  - (Chen, 2011).
- Data point estimated from Nikolaou et al., 2001

Chen, B. Y. "Hydrolytic Stabilities of Halogenated Disinfection Byproducts: Review and Rate Constant Quantitative Structure-Property Relationship Analysis." Environmental Engineering Science 28(6): 385-394.

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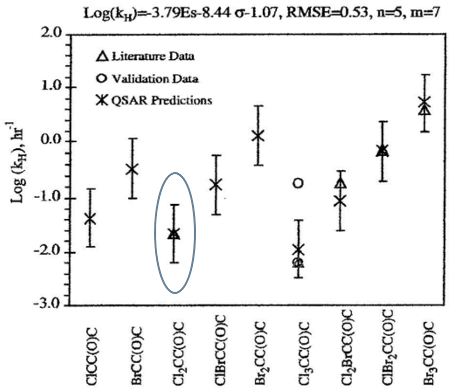

FIG. 4. Comparison of predicted (*) and literature (△, ○) data for hydrolysis rate constant (k_H) of haloketones. "n" denotes the number of DBP species for model calibration; "m" denotes number of literature data for model calibration and validation (see Table 1 for details); error bars indicate the 95% confidence intervals of calibrated model.

Comparison with Chen 2001

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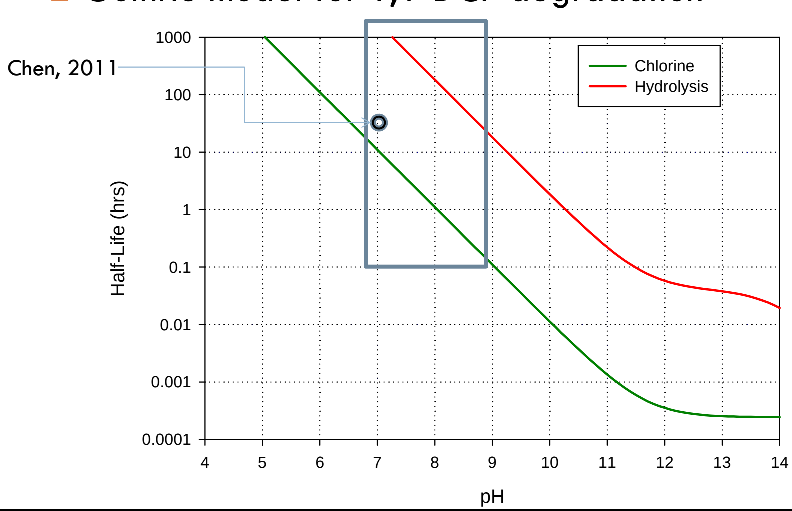
- Guthrie model for 1,1-DCP degradation



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Loss in water heaters

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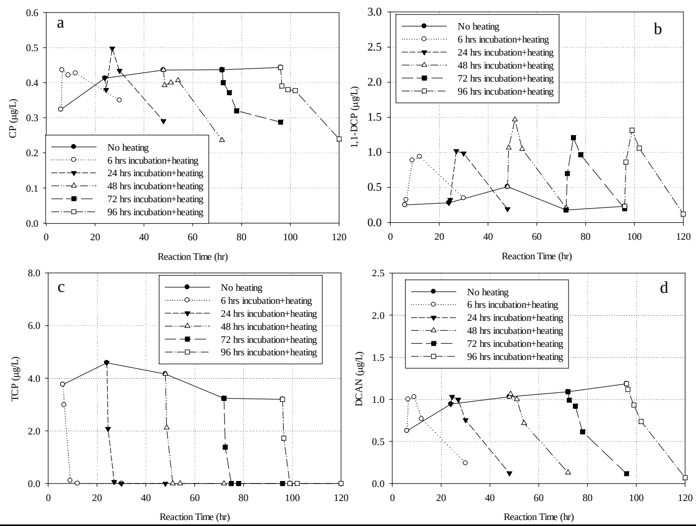
- Liu et al., 2013
  - In review



Profile of 1,1-DCP in Water Systems

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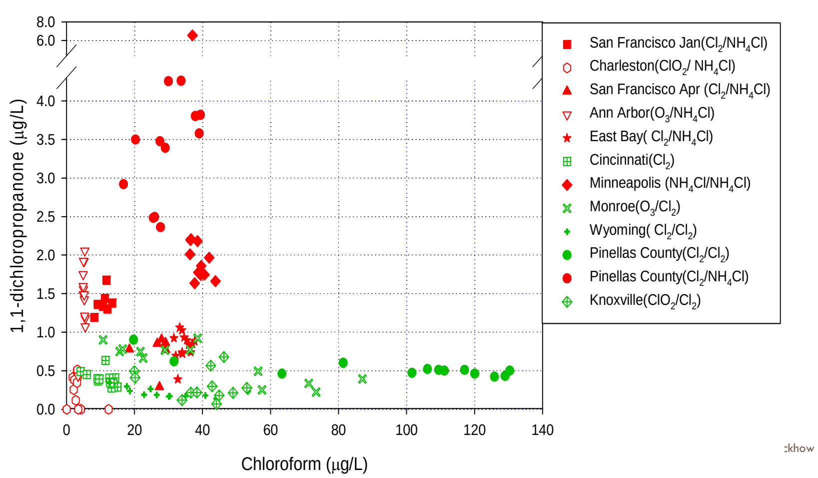
- 1,1-Dichloropropanone concentrations compared to the corresponding TTHM concentration for all samples



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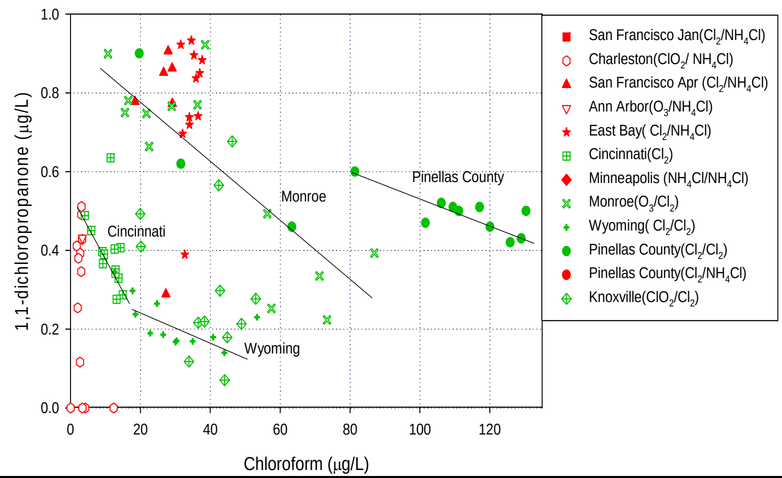
- 1,1-Dichloropropanone concentrations compared to the corresponding TTHM concentration for all samples: focus on free chlorine plants



Profile of TCP in water systems

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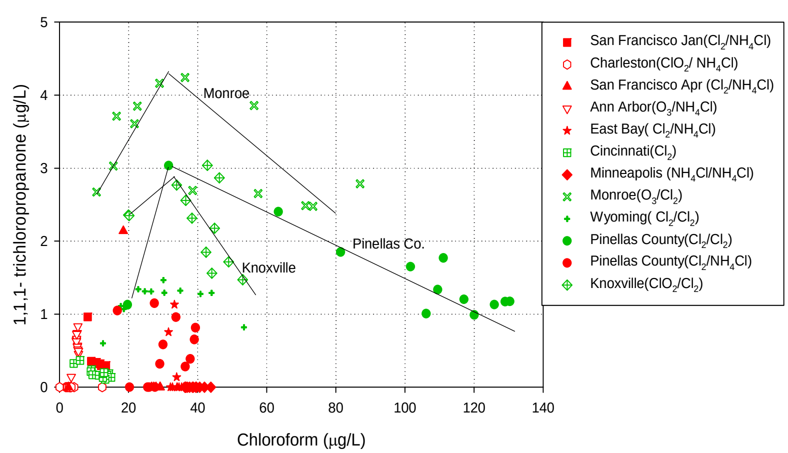
- **1,1,1-Trichloropropanone concentrations compared to the corresponding TTHM concentration for all samples**



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Lab 2

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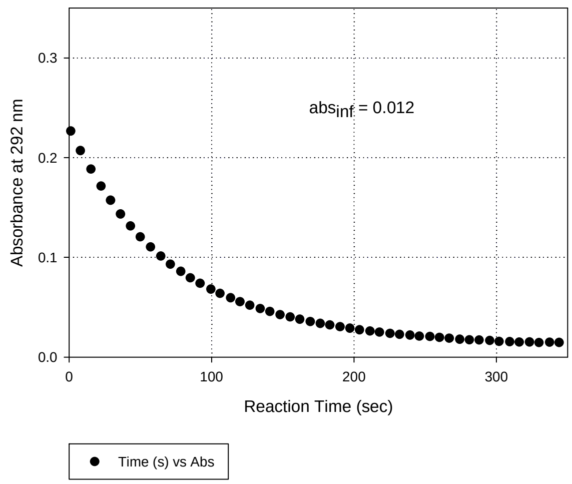
- 15 Oct 2013 experiment



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Lab 2

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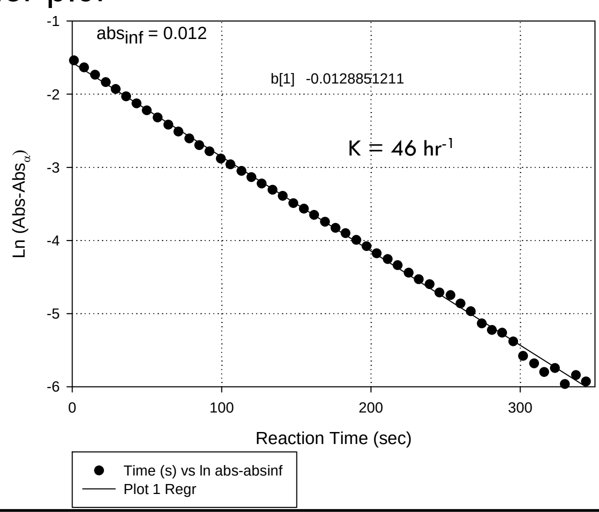
- 1st order plot



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Lab 2

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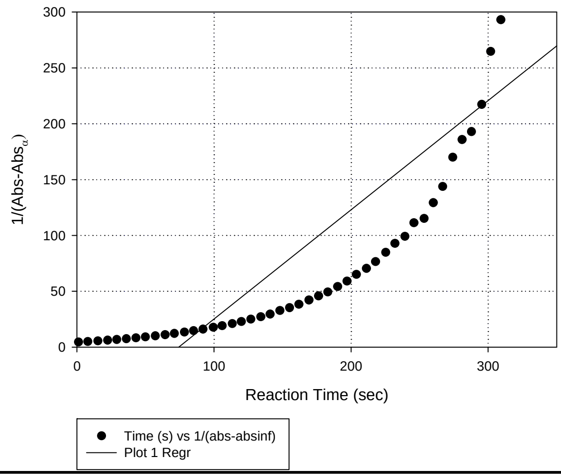
- 2nd order plot



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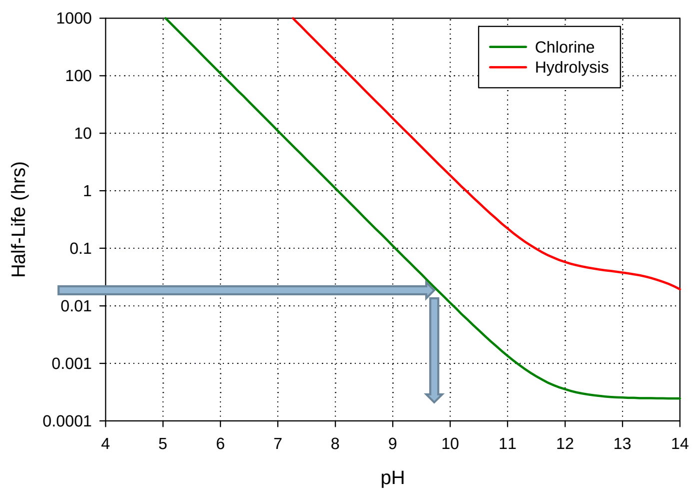
- Guthrie model



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- To next lecture