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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

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

Western Science

- 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

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.**

Mechanisms: Haloform Reaction

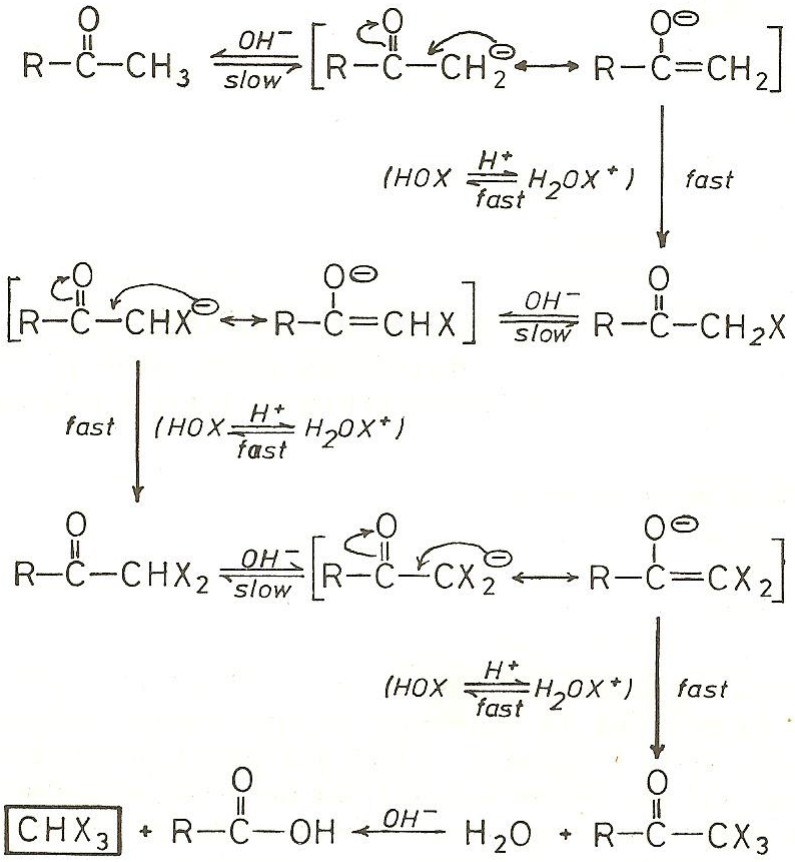


Figure 1. The reaction pathway of the haloform reaction.

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

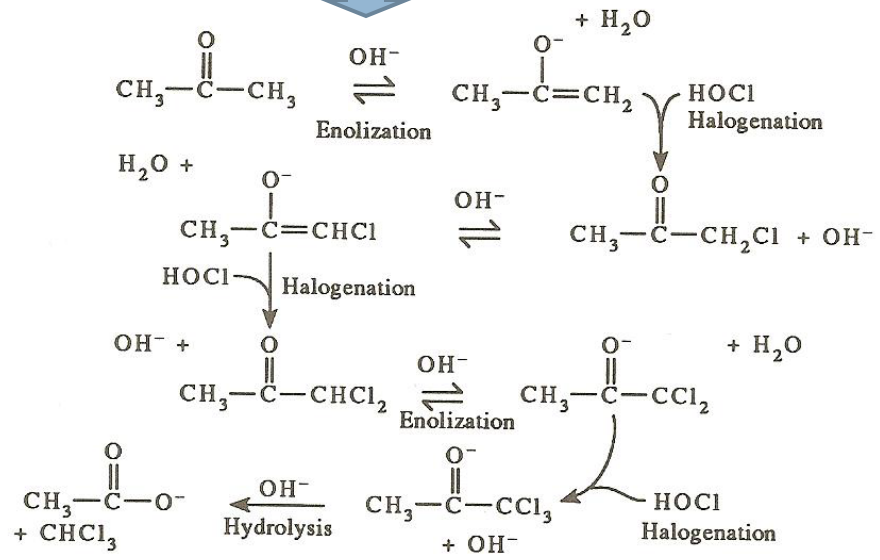


Figure 4-25. Reaction scheme for production of chloroform from acetone by the classic haloform reaction.

Haloform reaction: initial step

- 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]

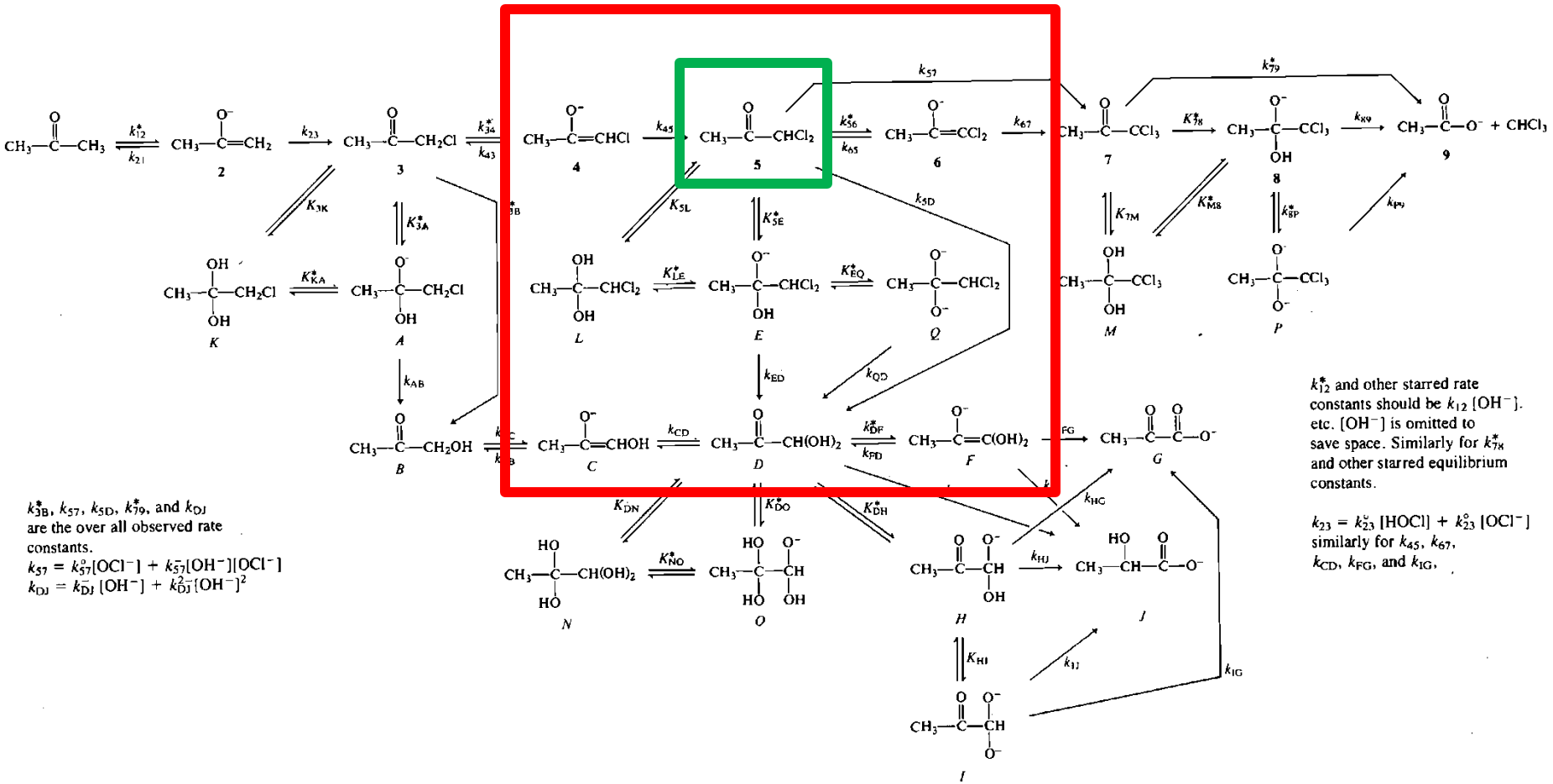
Substance	pK_a	K_O sec^{-1}	K_{OH} 1/mol, sec	K_H 1/mol, sec	t_{50} pH 7, hr	t_{50}, pH 8.3 hr
Acetone	20	4.7×10^{-10}	0.25	2.9×10^{-5}	7500	385
Chloroacetone	16.5	5.3×10^{-8}	93	6.3×10^{-5}	21	1.0
as-Dichloroacetone	15	7.3×10^{-6}	450	1.1×10^{-5}	3.7	0.21
Pyruvic acid[6]		4.5×10^{-7}				
Ethyl pyruvate[6]	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?

Guthrie & Cossar Pathway

- Scheme 1

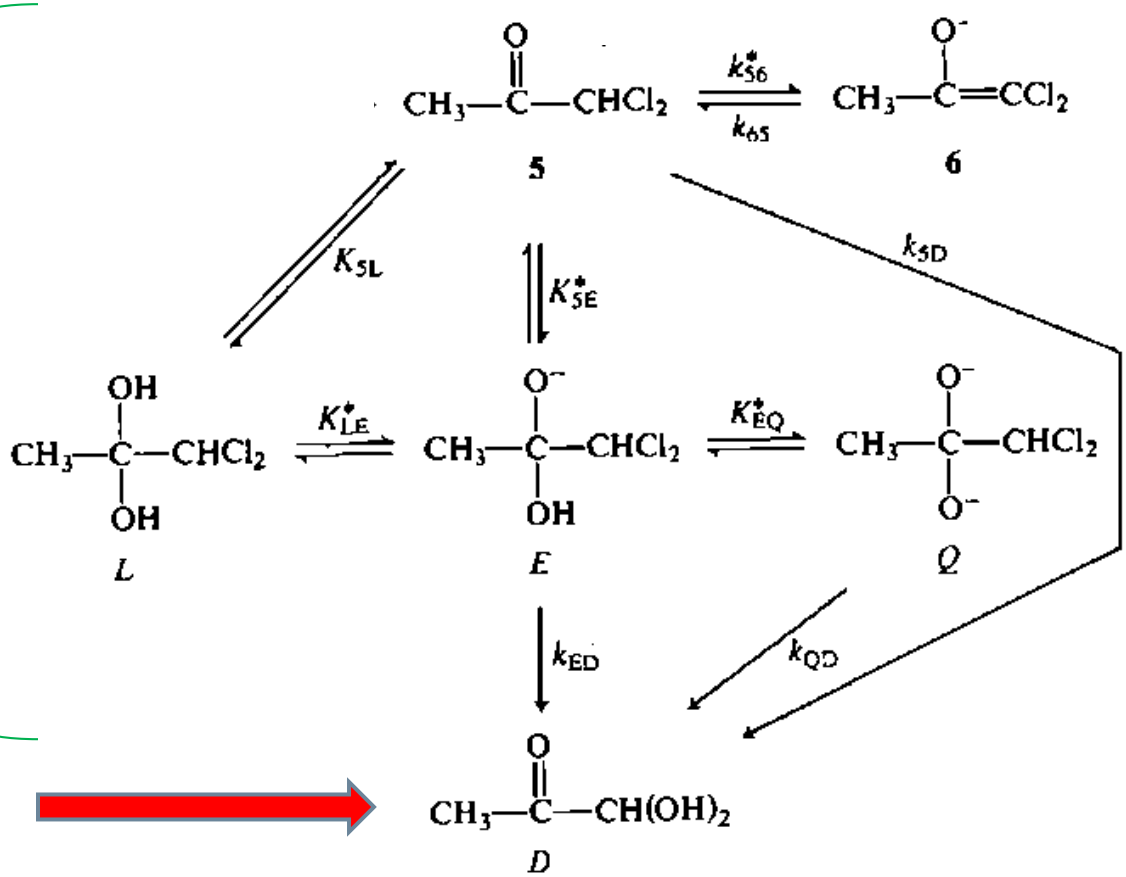


SCHEME 1.

Hydrolysis of 1,1-DCP

- a

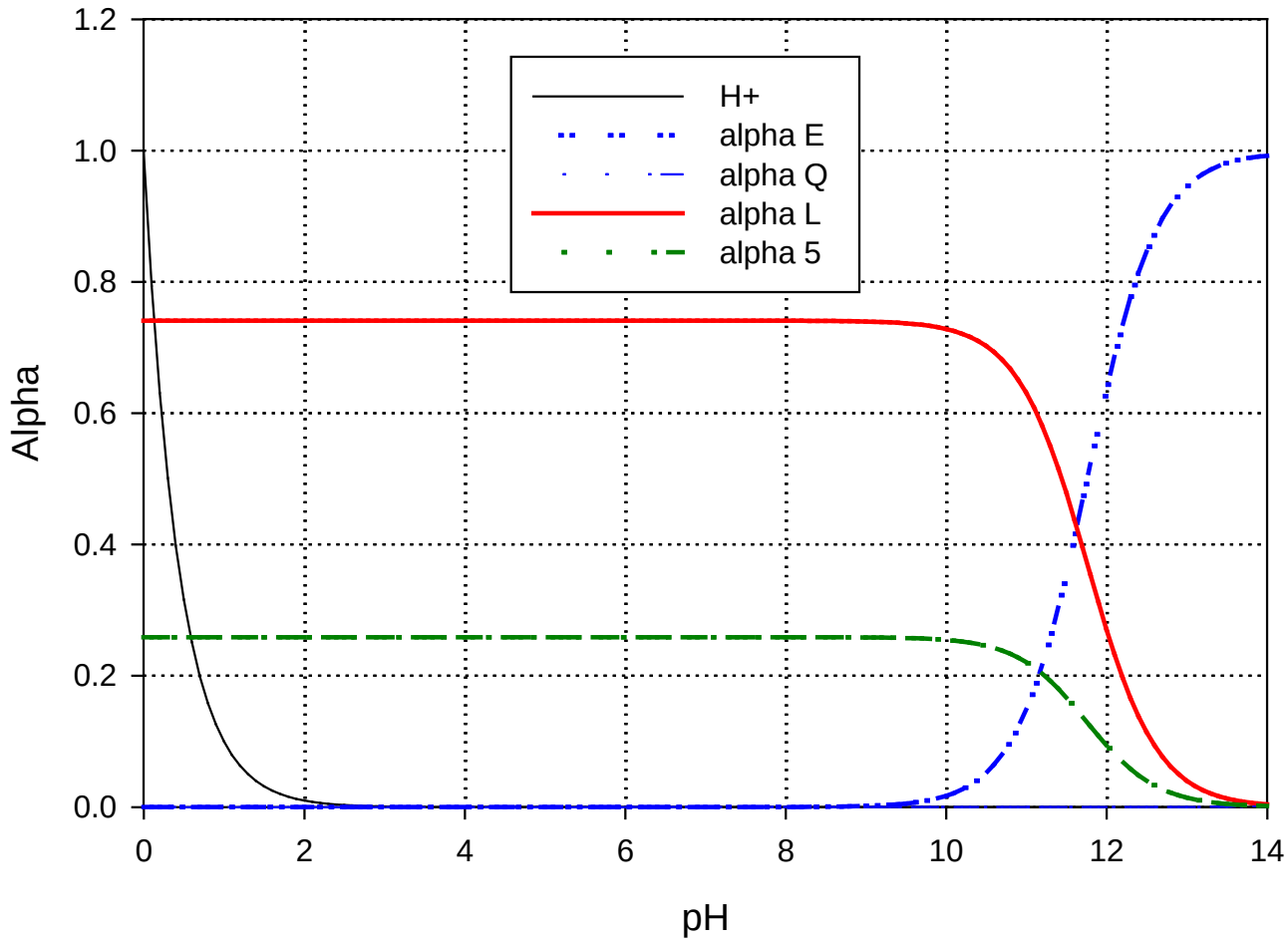
The many forms of 1,1-DCP



The product

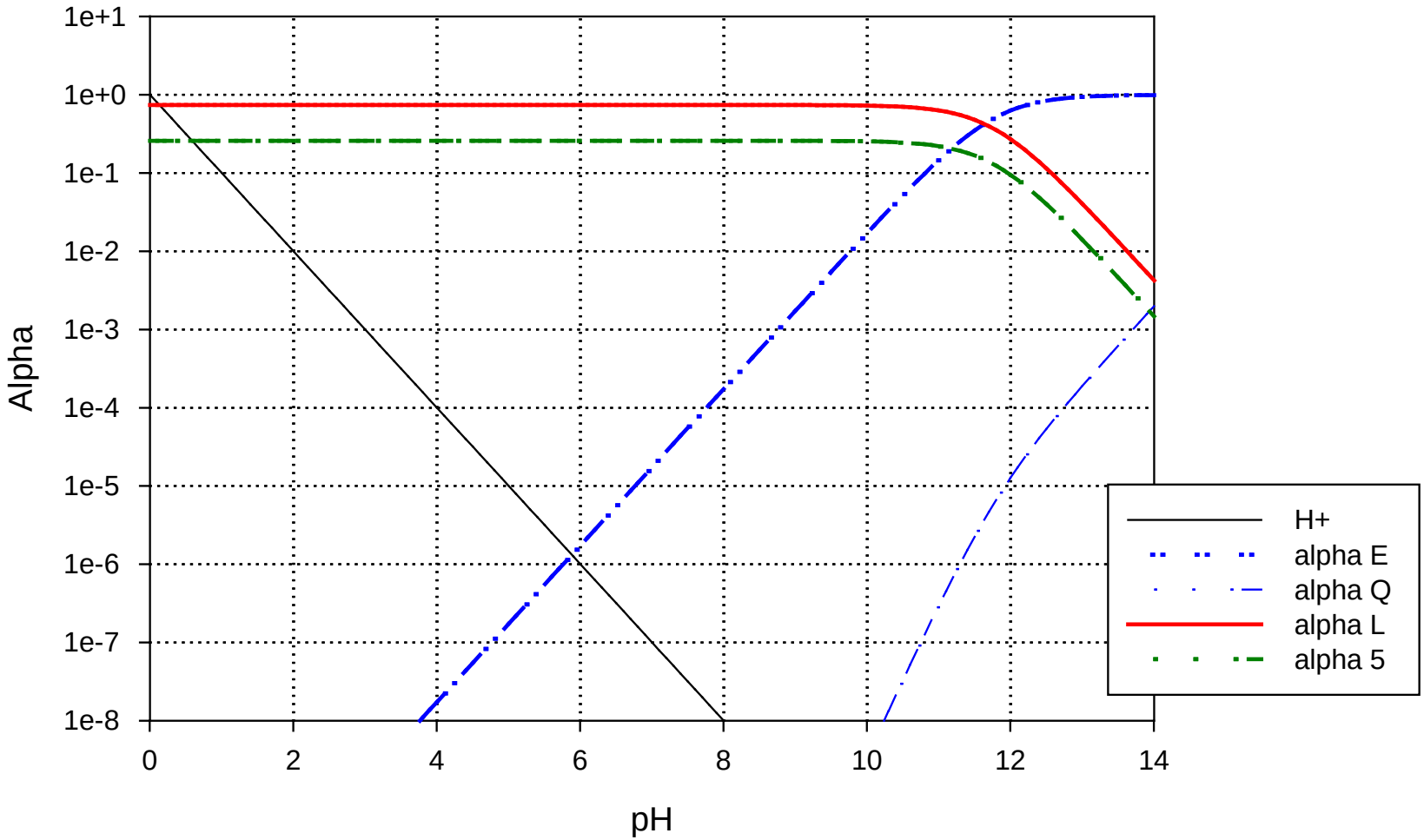
DCP equilibria I

- Bell K's



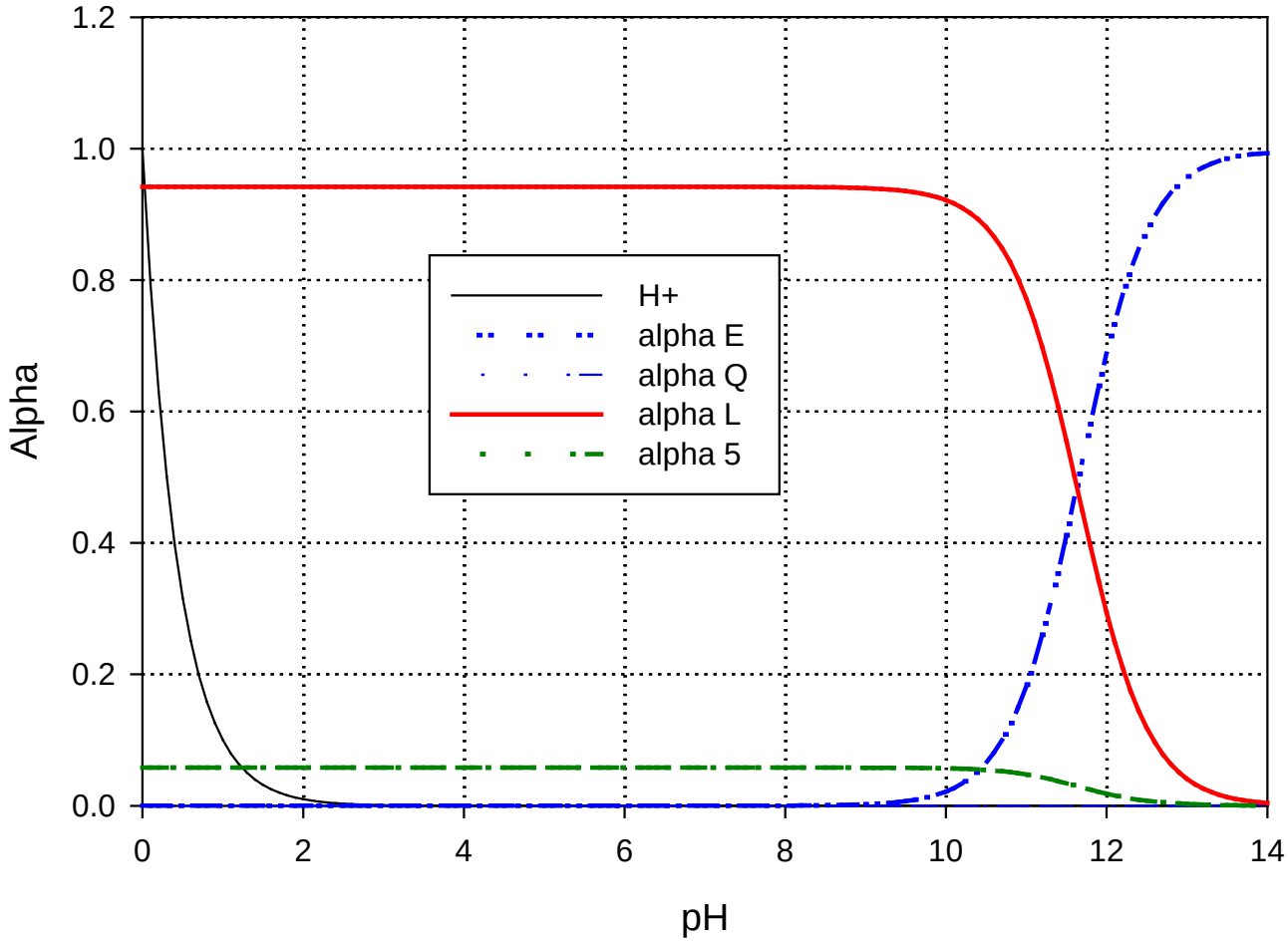
DCP equilibria II

- Bell K's



DCP equilibria III

- Guthrie K's



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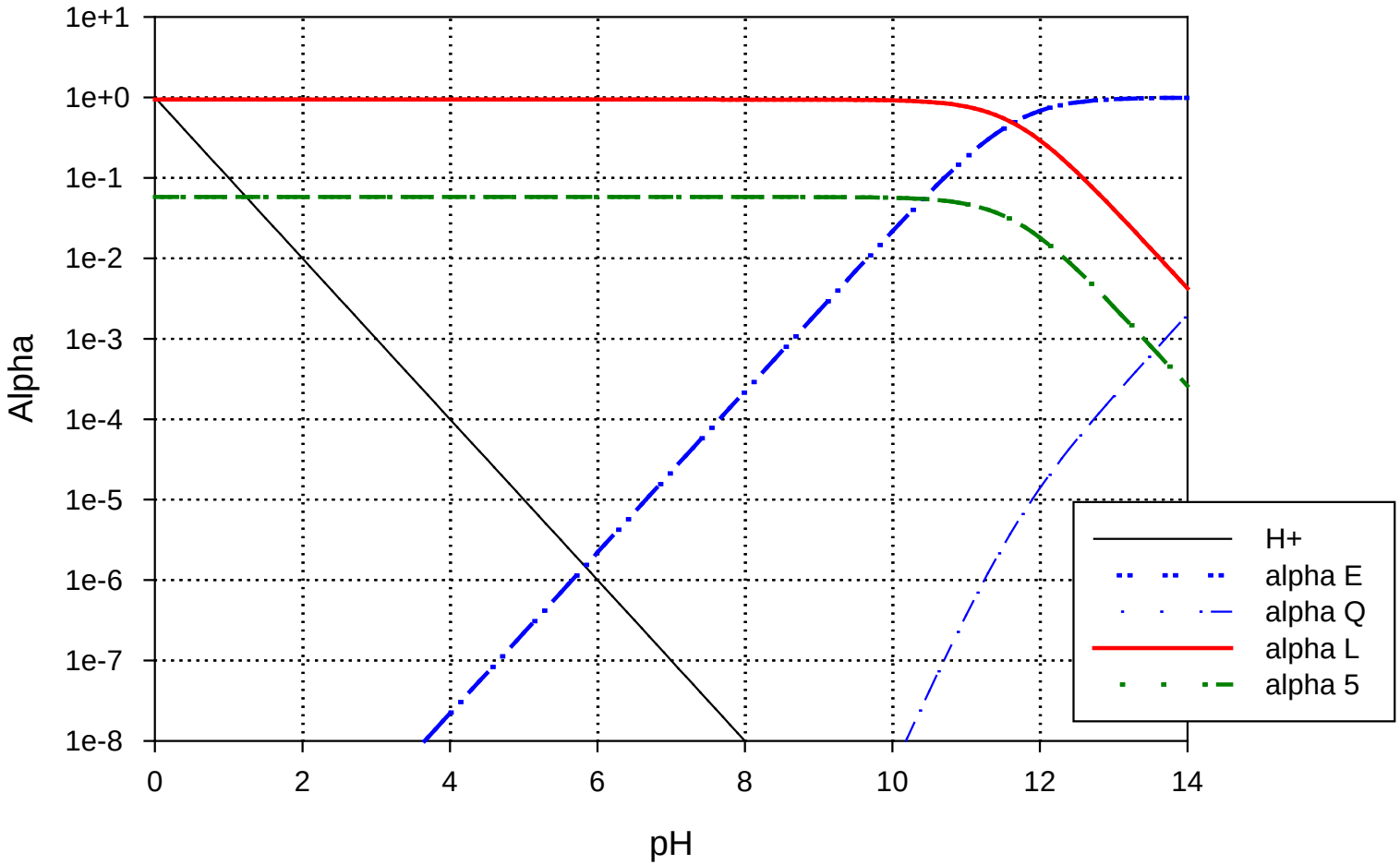
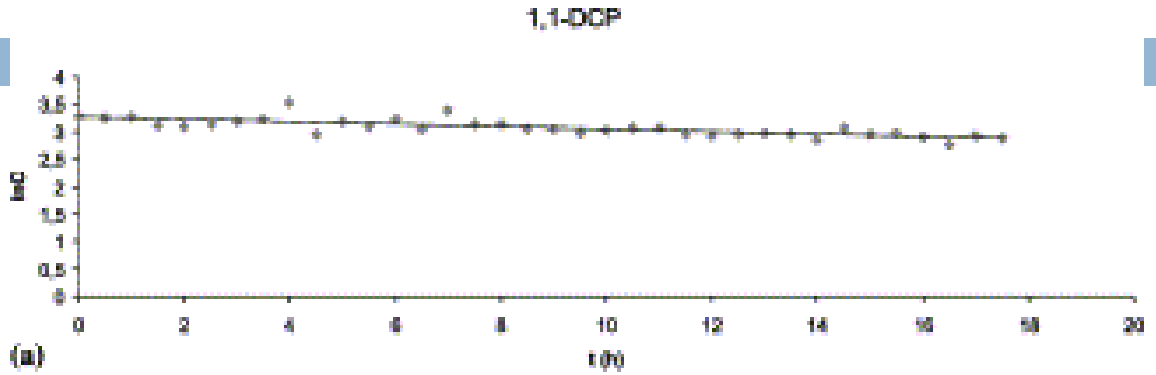
DCP equilibria IV

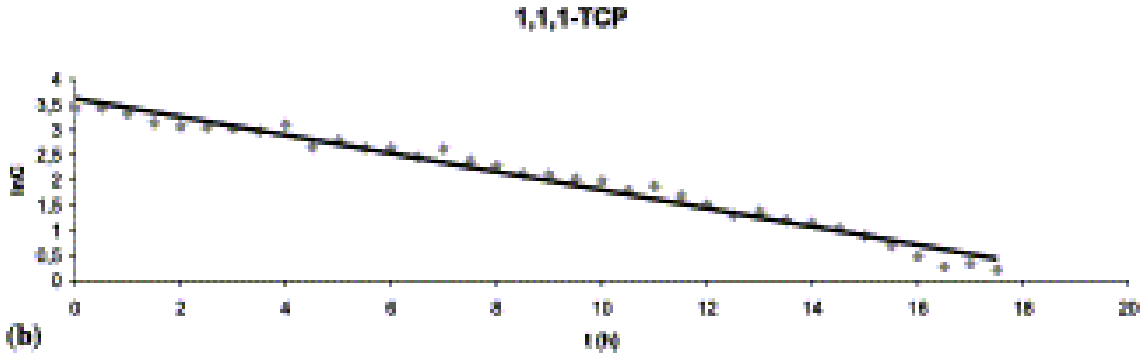
- Guthrie K's

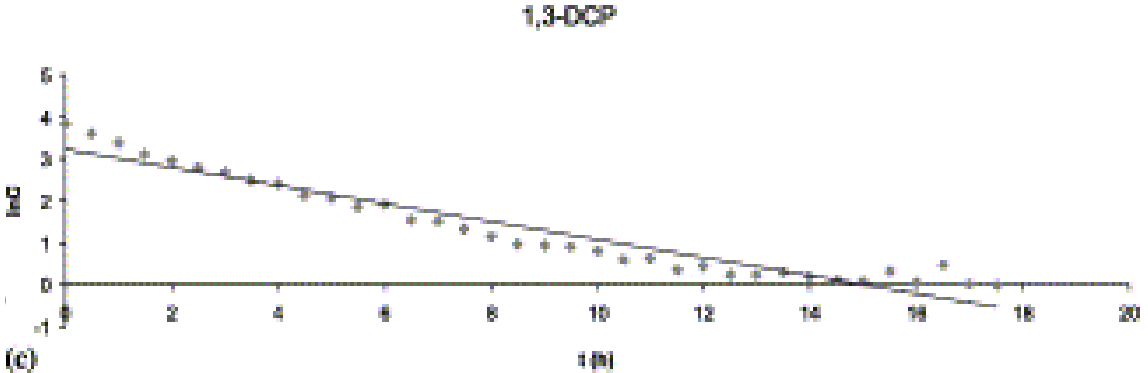


Loss of intermediates in lab water

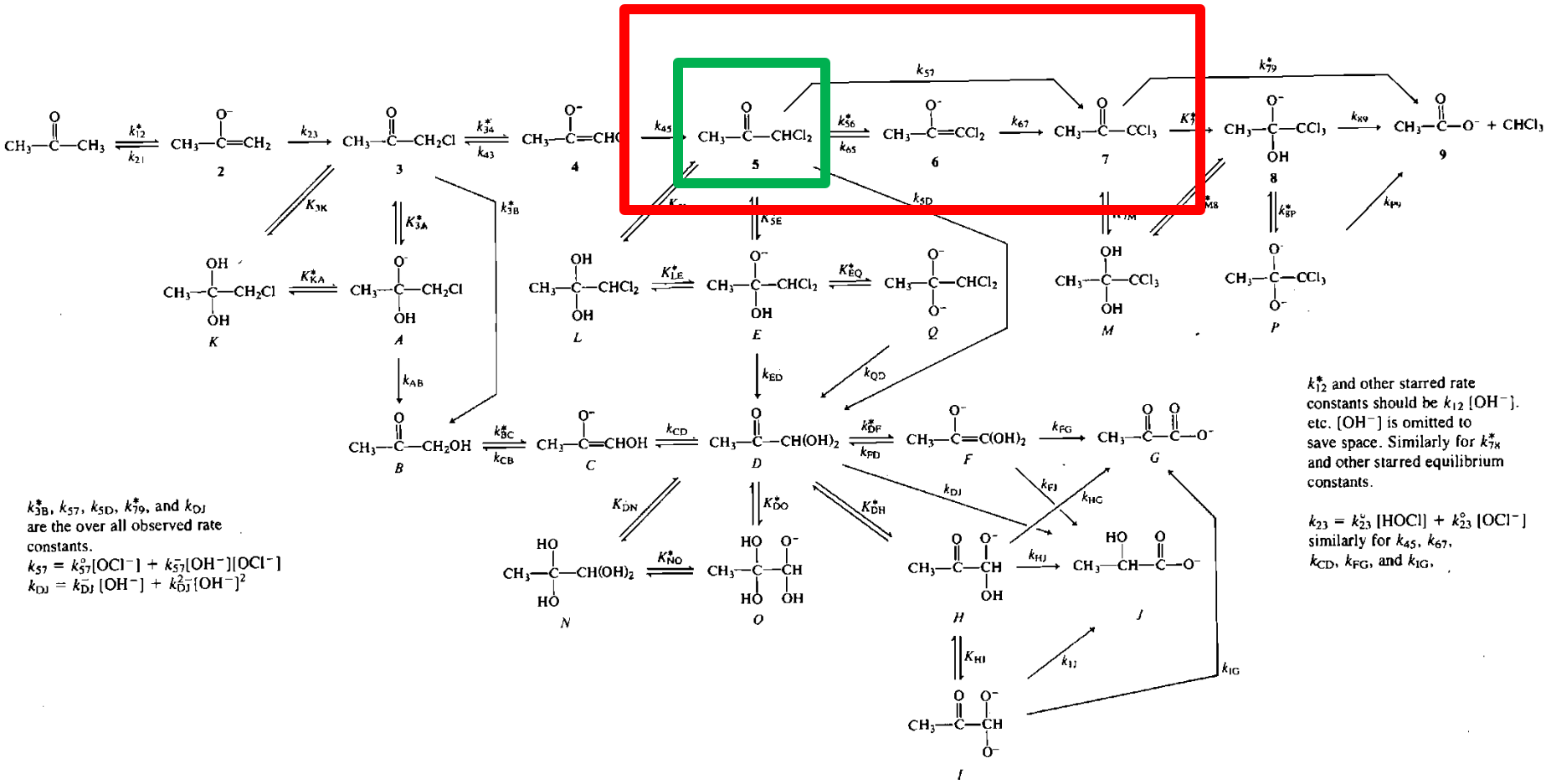
- 21C, ultrapure water
  - (Nikolaou et al., 2001)







chlorine



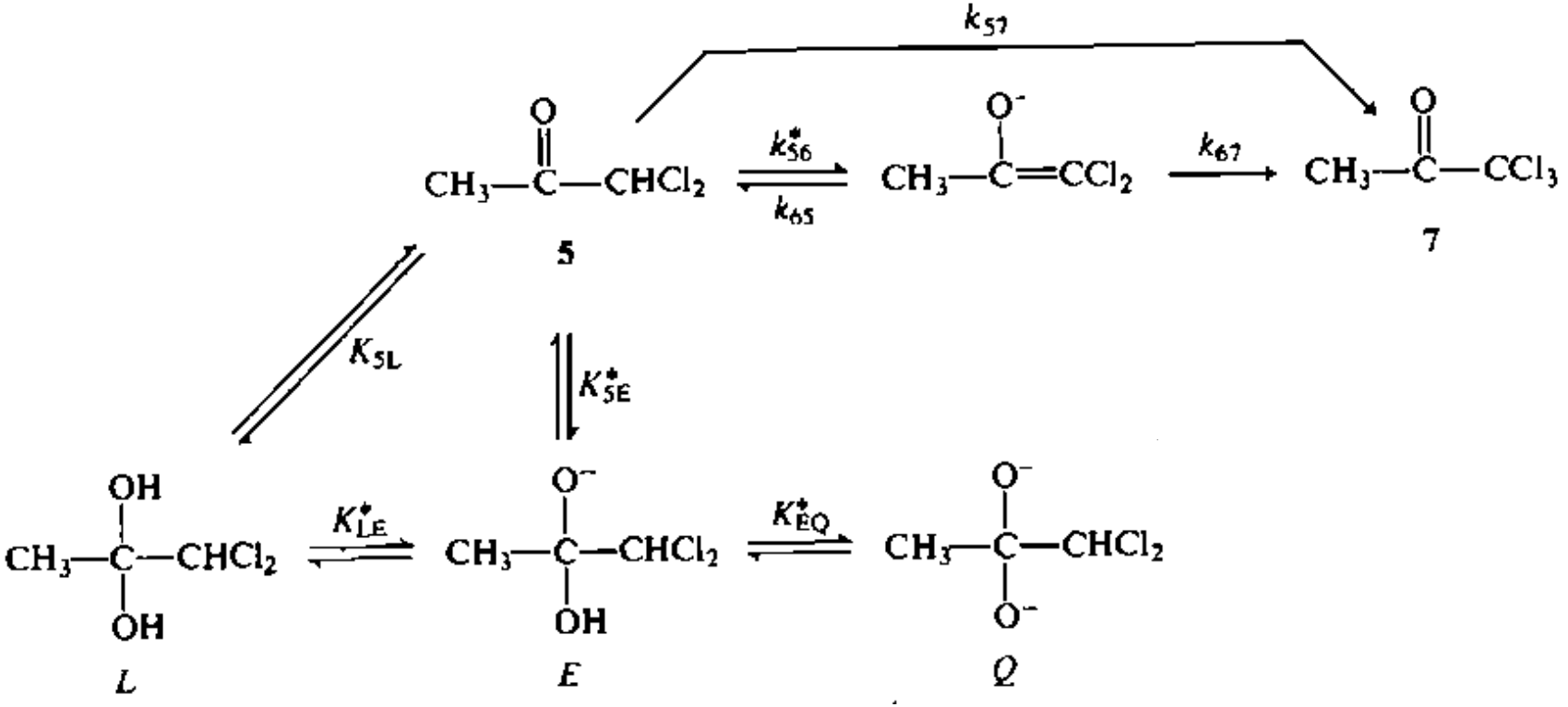
k^*_{3B}, k_{57}, k_{5D}, k^*_{79}, and k_{DJ} are the over all observed rate constants.
$k_{57} = k^\circ_{57}[OCl^-] + k^-_{57}[OH^-][OCl^-]$
$k_{DJ} = k^-_{DJ}[OH^-] + k^2_{DJ}[OH^-]^2$

k^*_{12} and other starred rate constants should be $k_{12}[OH^-]$. etc. $[OH^-]$ is omitted to save space. Similarly for k^*_{78} and other starred equilibrium constants.

$k_{23} = k^\circ_{23}[HOCl] + k^\circ_{23}[OCl^-]$ similarly for k_{45}, k_{67}, k_{CD}, k_{FG}, and k_{IG}.

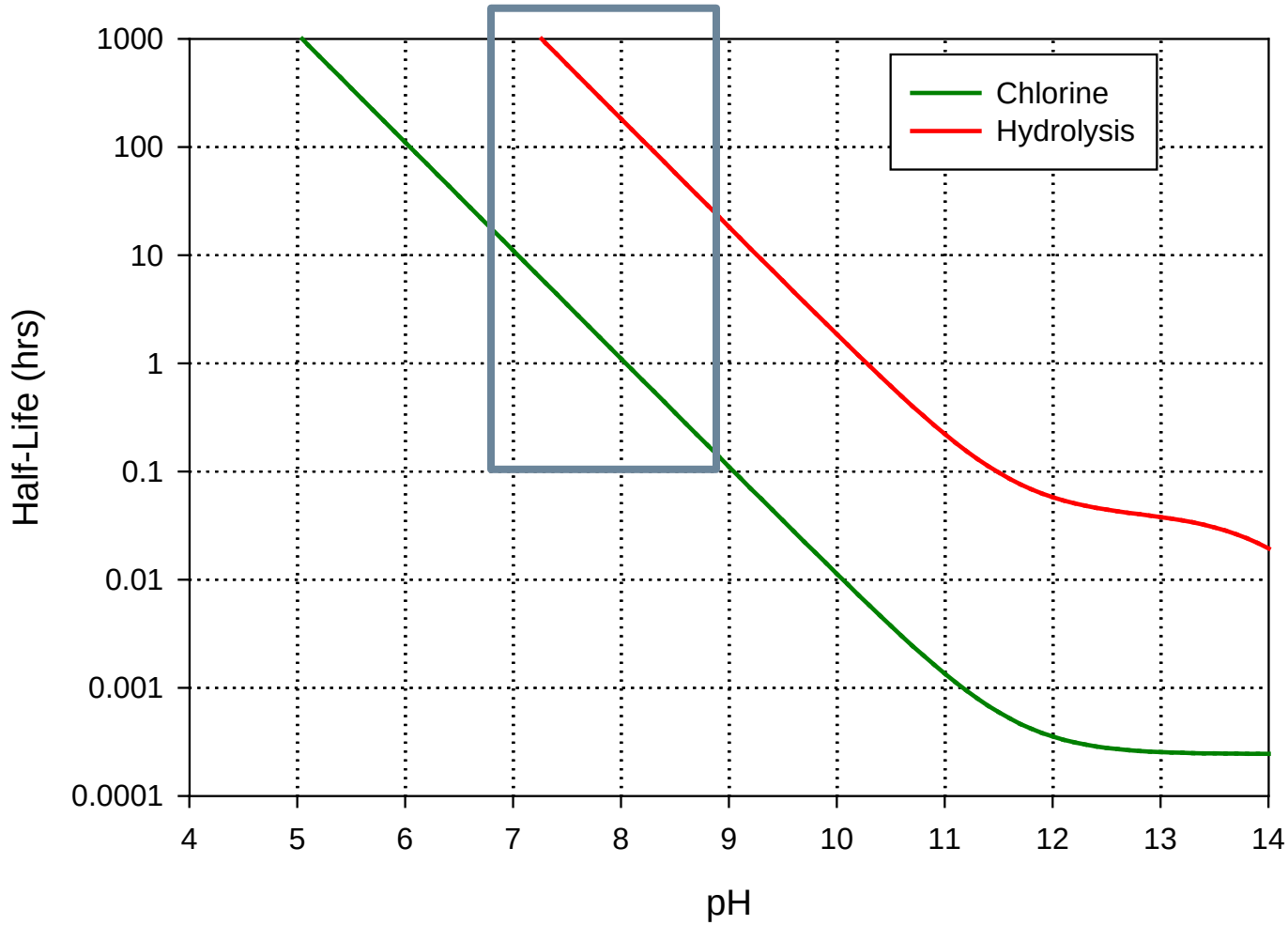
SCHEME 1.

- a


k_{57}
$CH_3-C(=O)-CHCl_2$
k_{56}^*
k_{65}
$CH_3-C(-O^-)=CCl_2$
k_{67}
$CH_3-C(=O)-CCl_3$
5
7
K_{5L}
K_{5E}^*
$CH_3-C(OH)(OH)-CHCl_2$
K_{LE}^*
$CH_3-C(-O^-)(OH)-CHCl_2$
K_{EQ}^*
$CH_3-C(-O^-)(-O^-)-CHCl_2$
L
E
Q

Model

- Guthrie model for 1,1-DCP degradation



LFER Analysis

- 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 x 10^{-6} sec^{-1}
  - (Chen, 2011).
- Data point estimated from Nikolaou et al., 2001

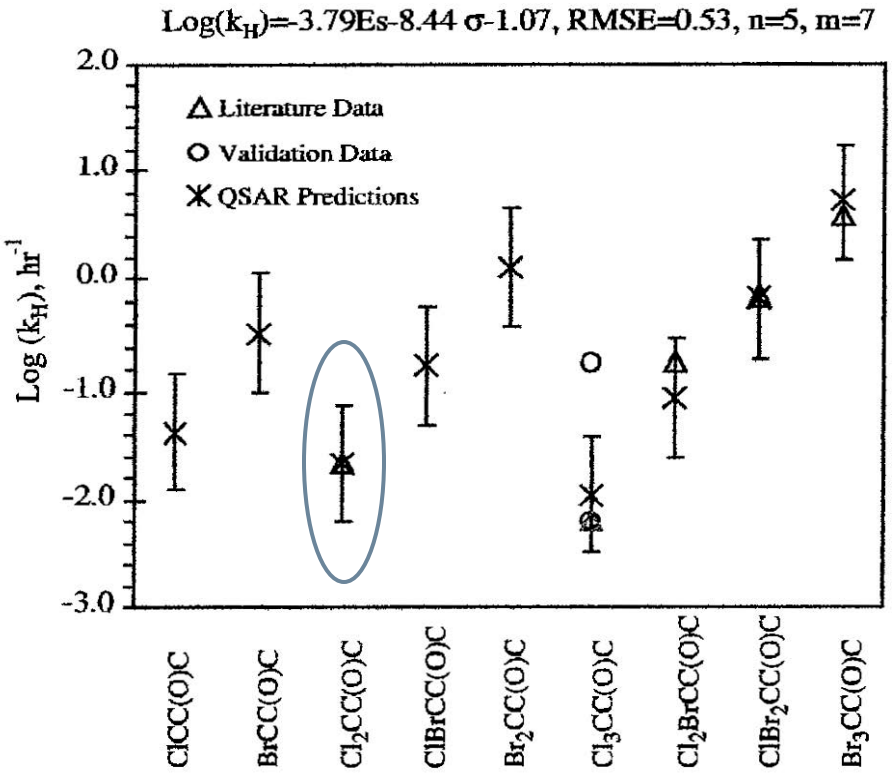
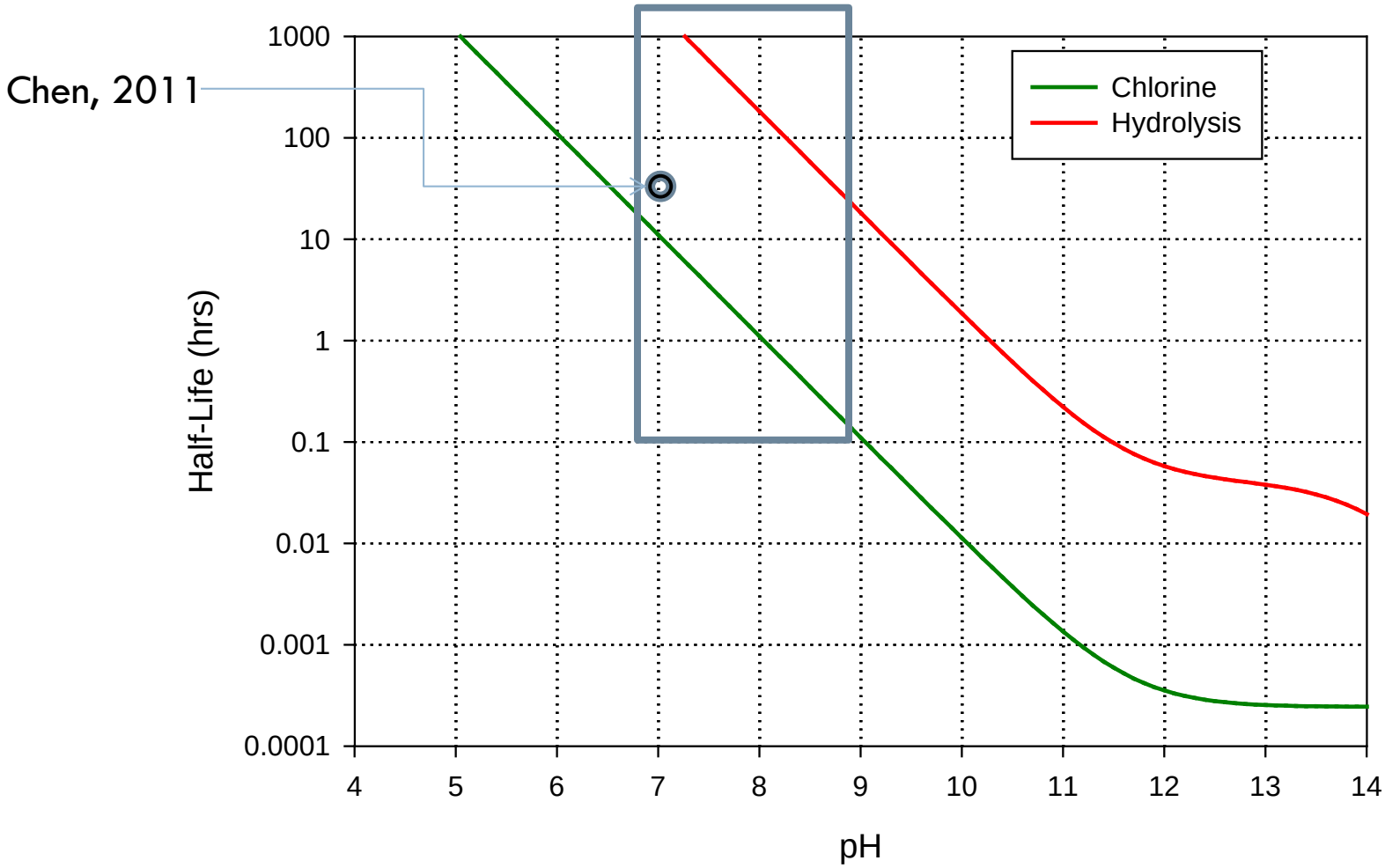


FIG. 4. Comparison of predicted (*) and literature (△, ○) data for hydrolysis rate constant (k_H) of haloketones. "n" denotes the number of DBP species for model calibration; "m" denotes number of literature data for model calibration and validation (see Table 1 for details); error bars indicate the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

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.**

Comparison with Chen 2001

- Guthrie model for 1,1-DCP degradation



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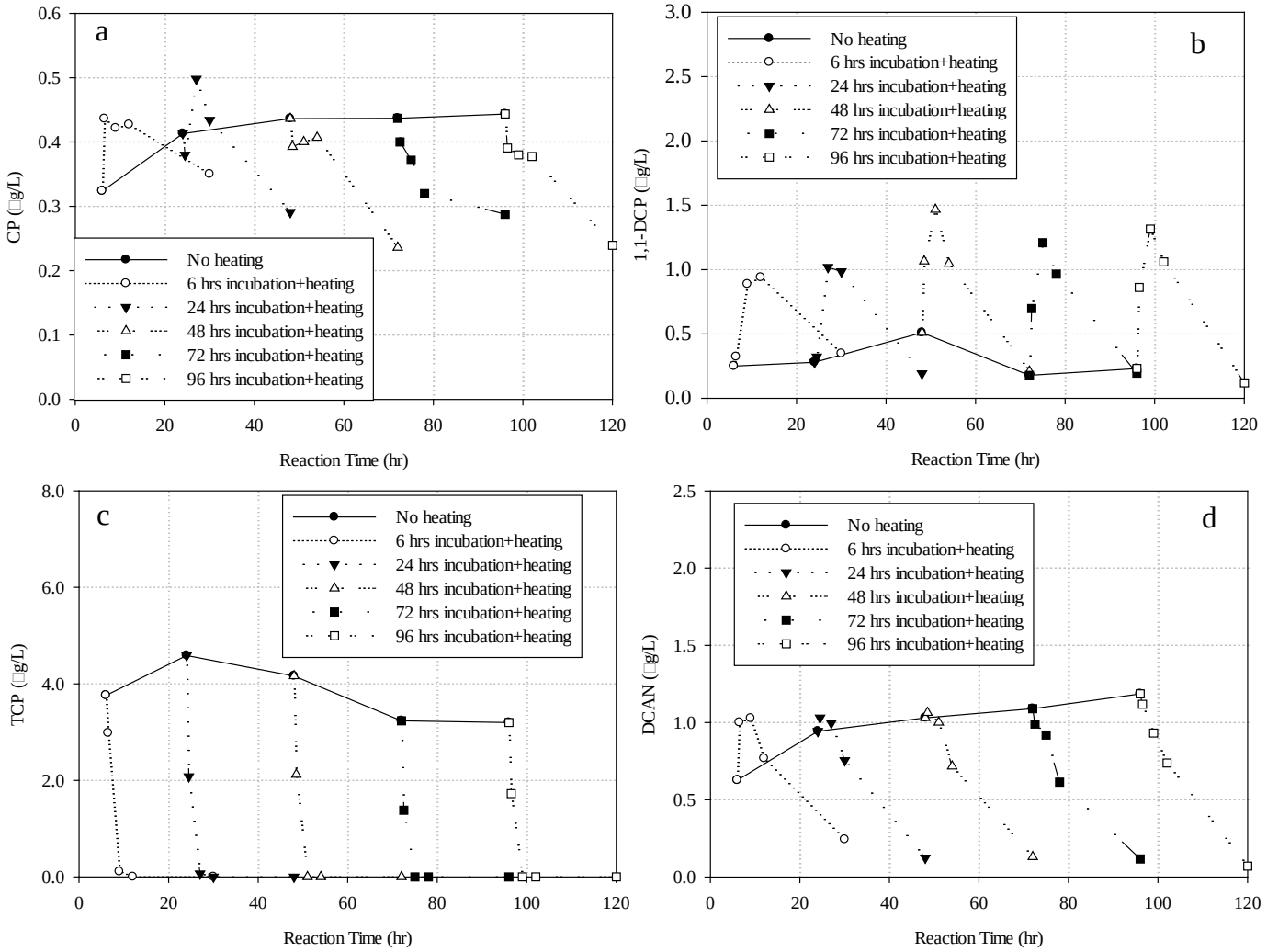
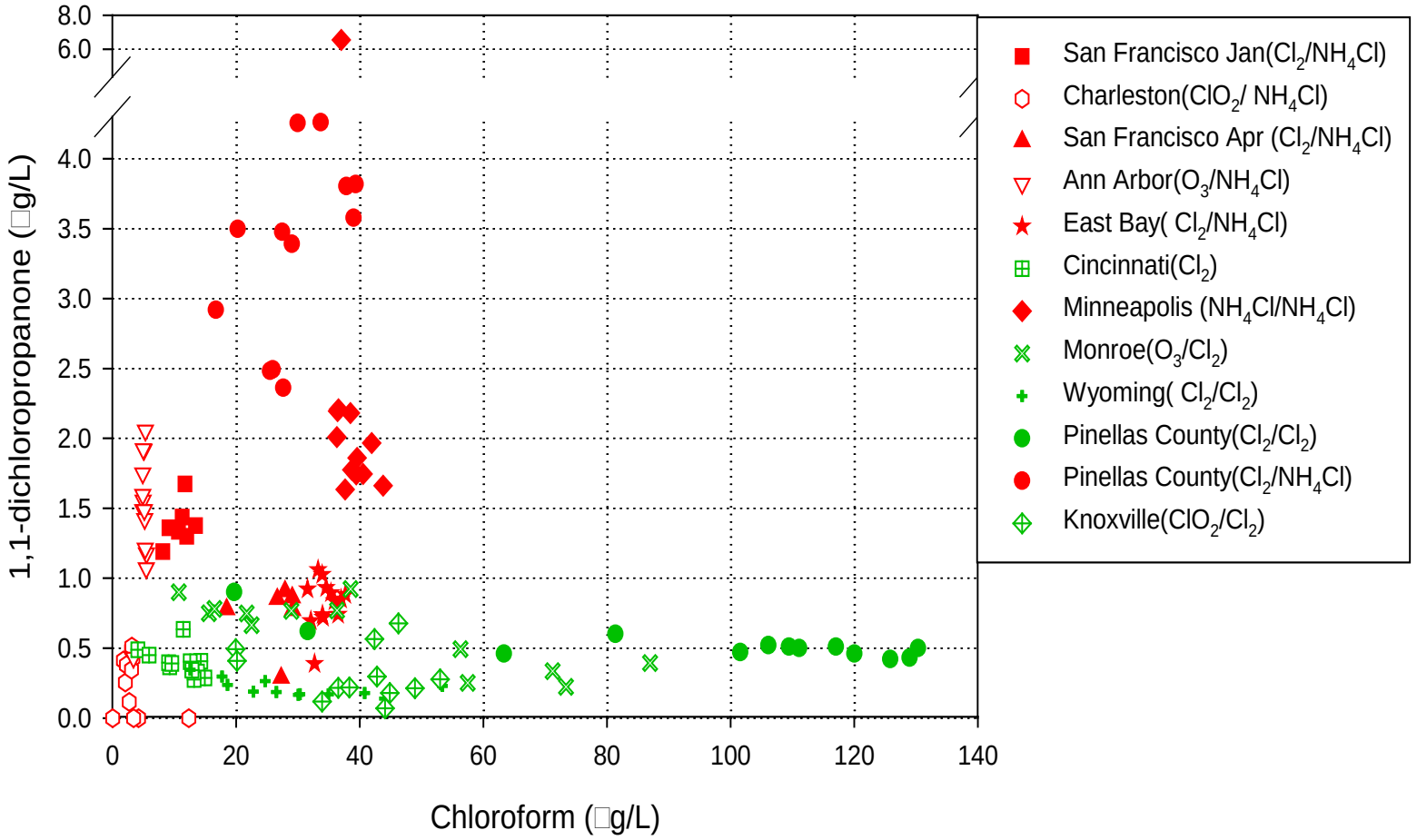
Loss in water heaters

- Liu et al., 2013
  - In review

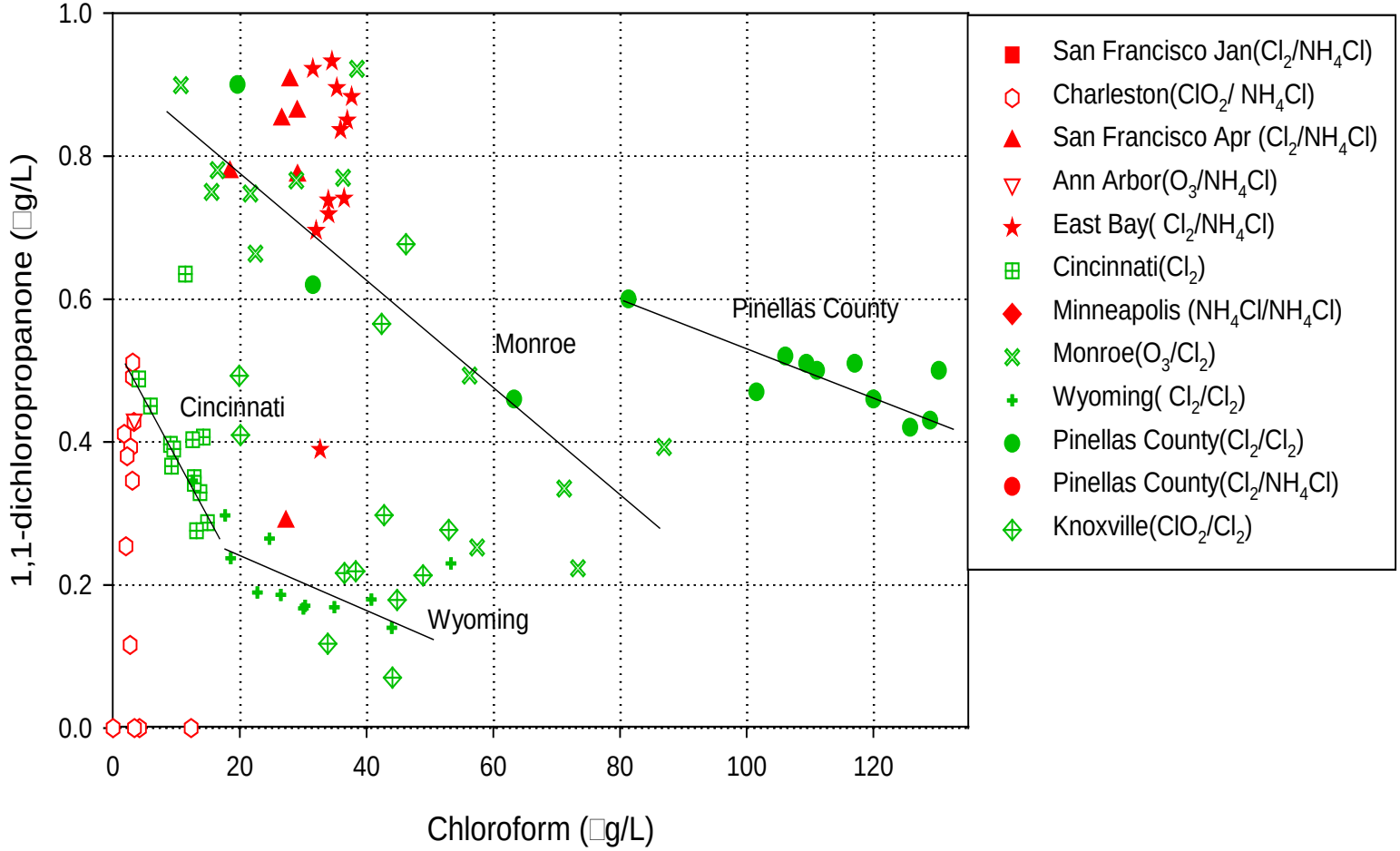


Profile of 1,1-DCP in Water Systems

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

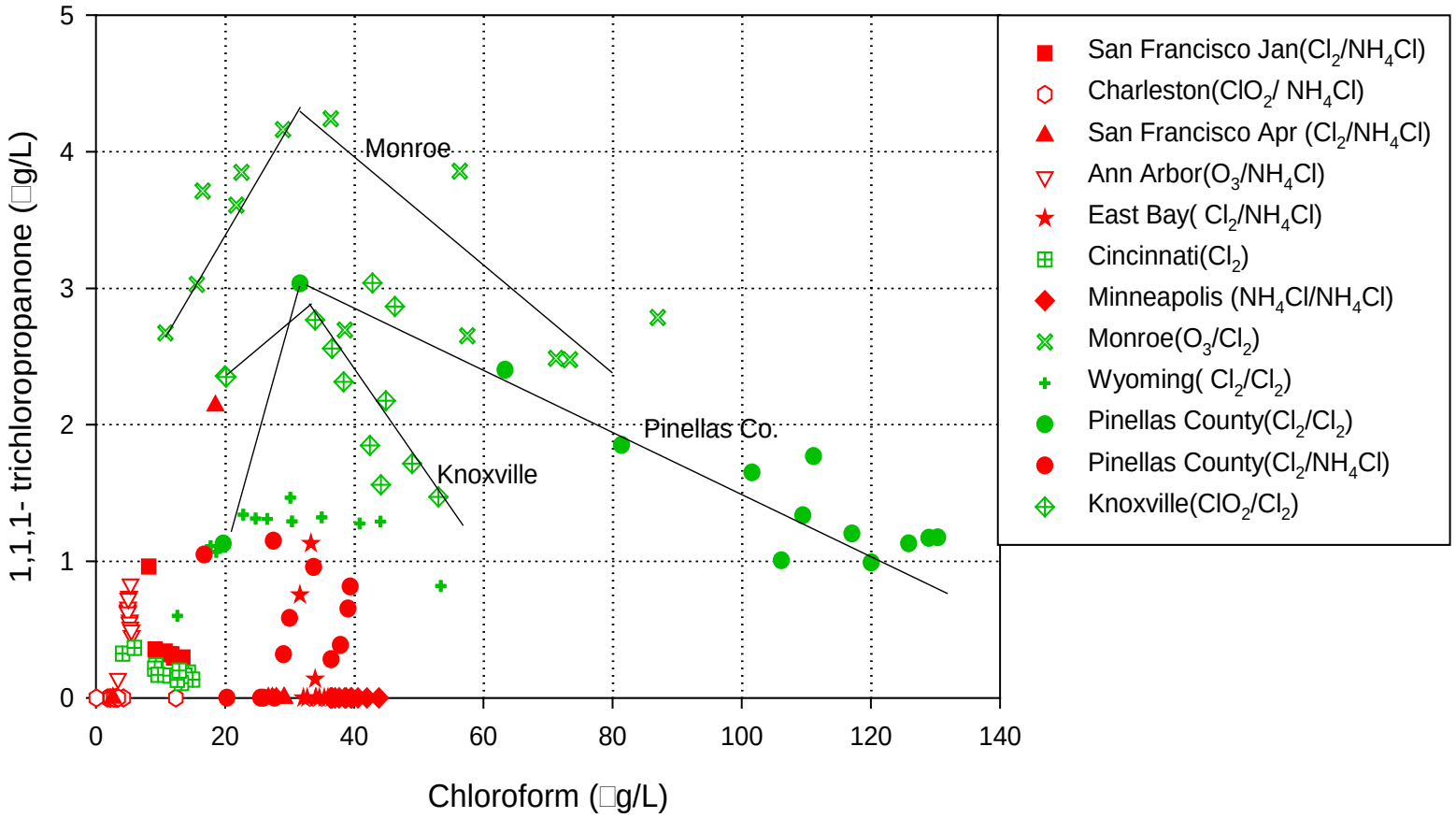


- 1,1-Dichloropropanone concentrations compared to the corresponding TTHM concentration for all samples: focus on free chlorine plants



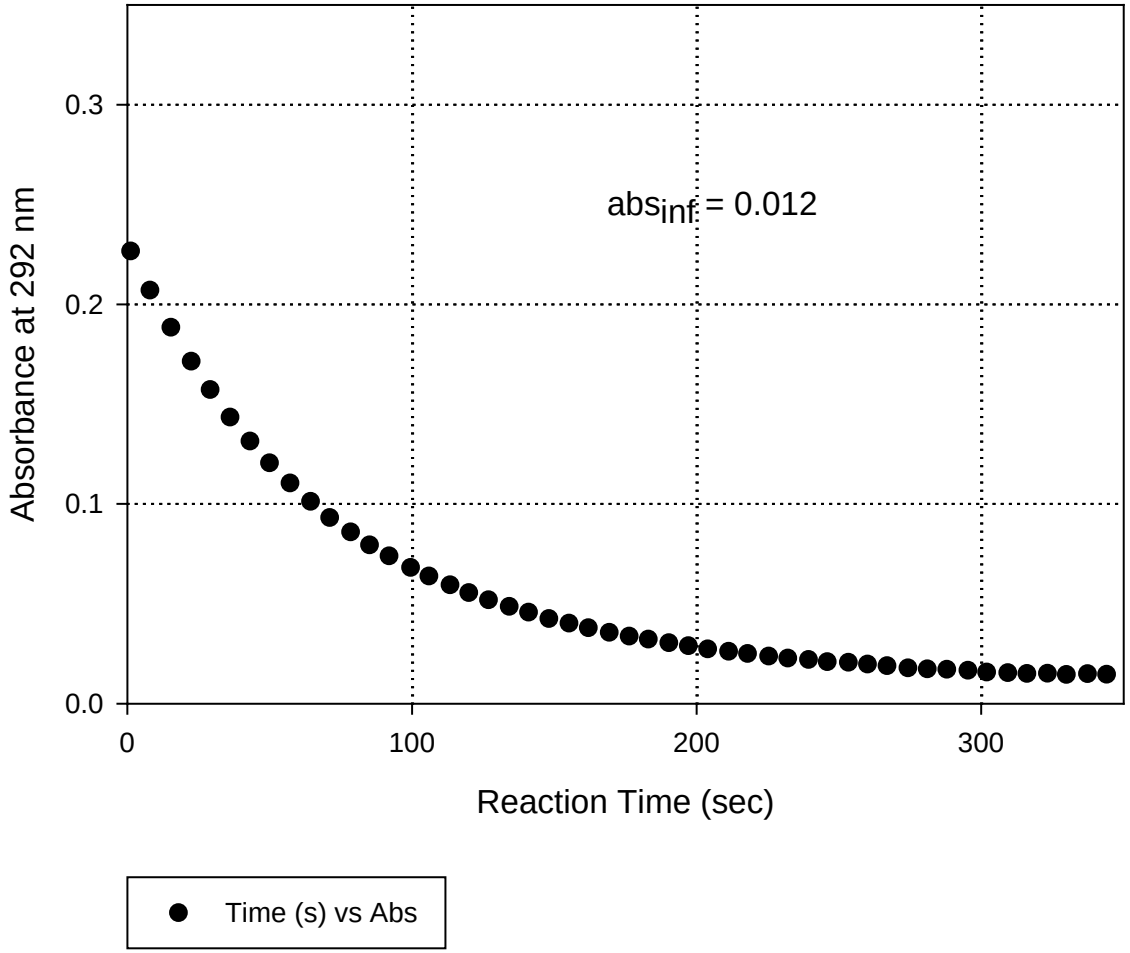
Profile of TCP in water systems

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



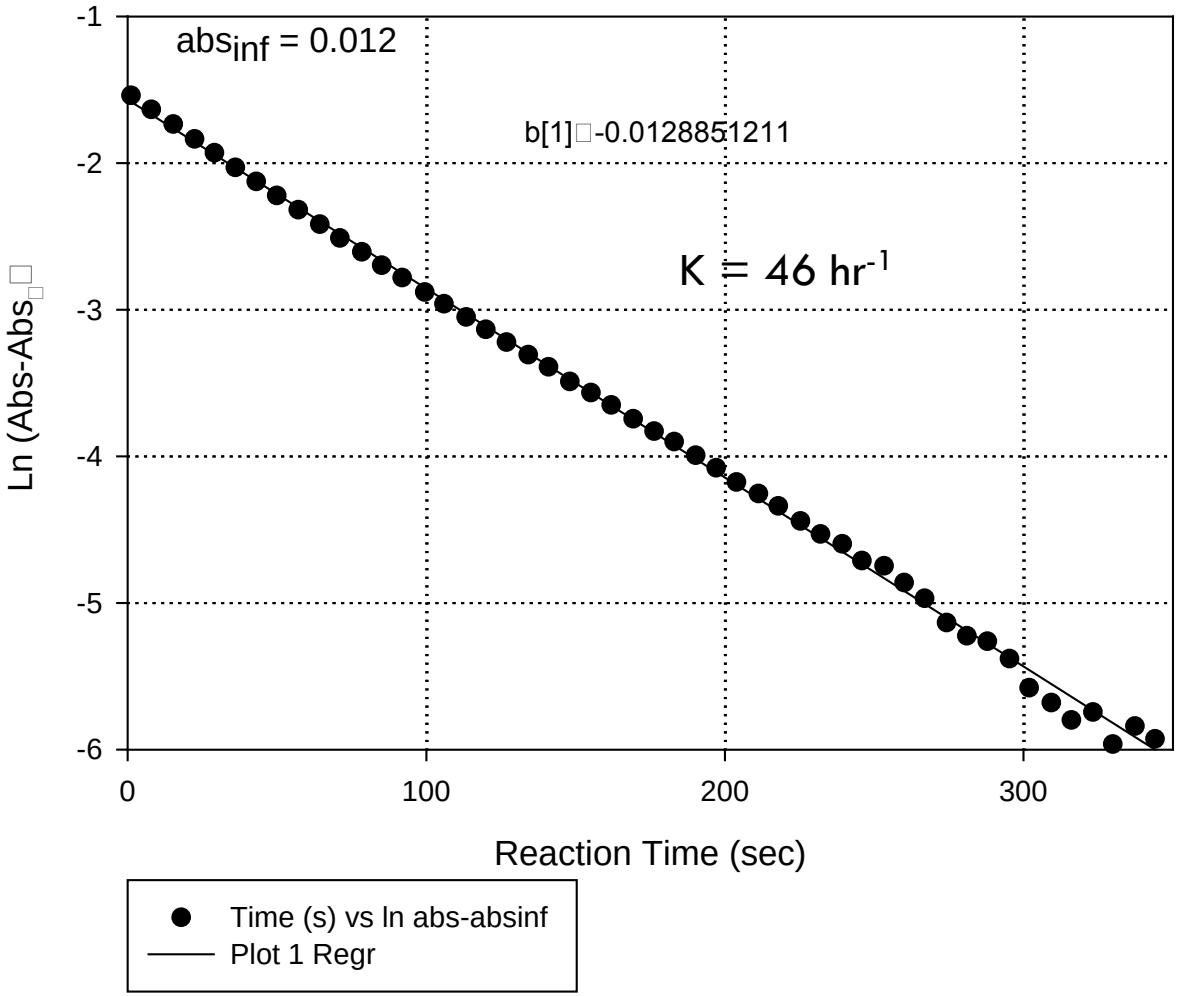
Lab 2

- 15 Oct 2013 experiment



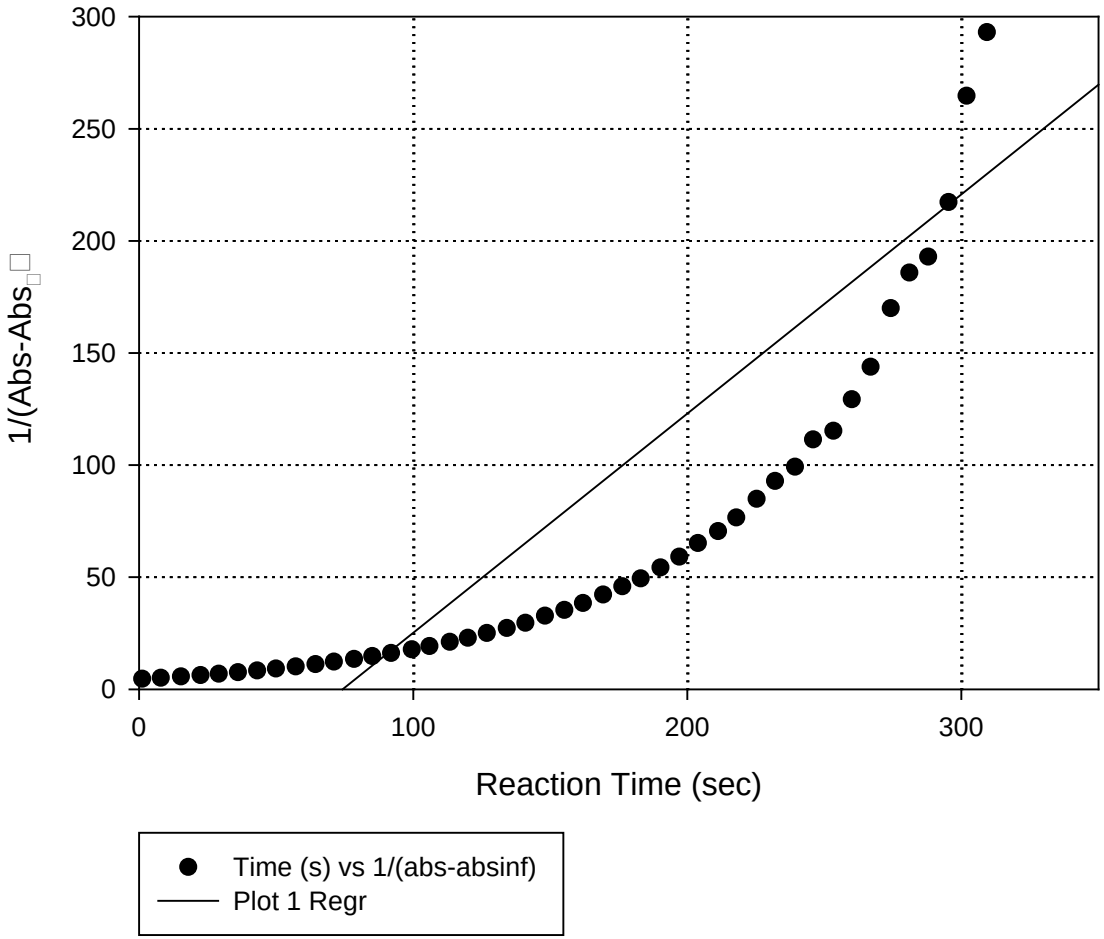
Lab 2

- 1st order plot

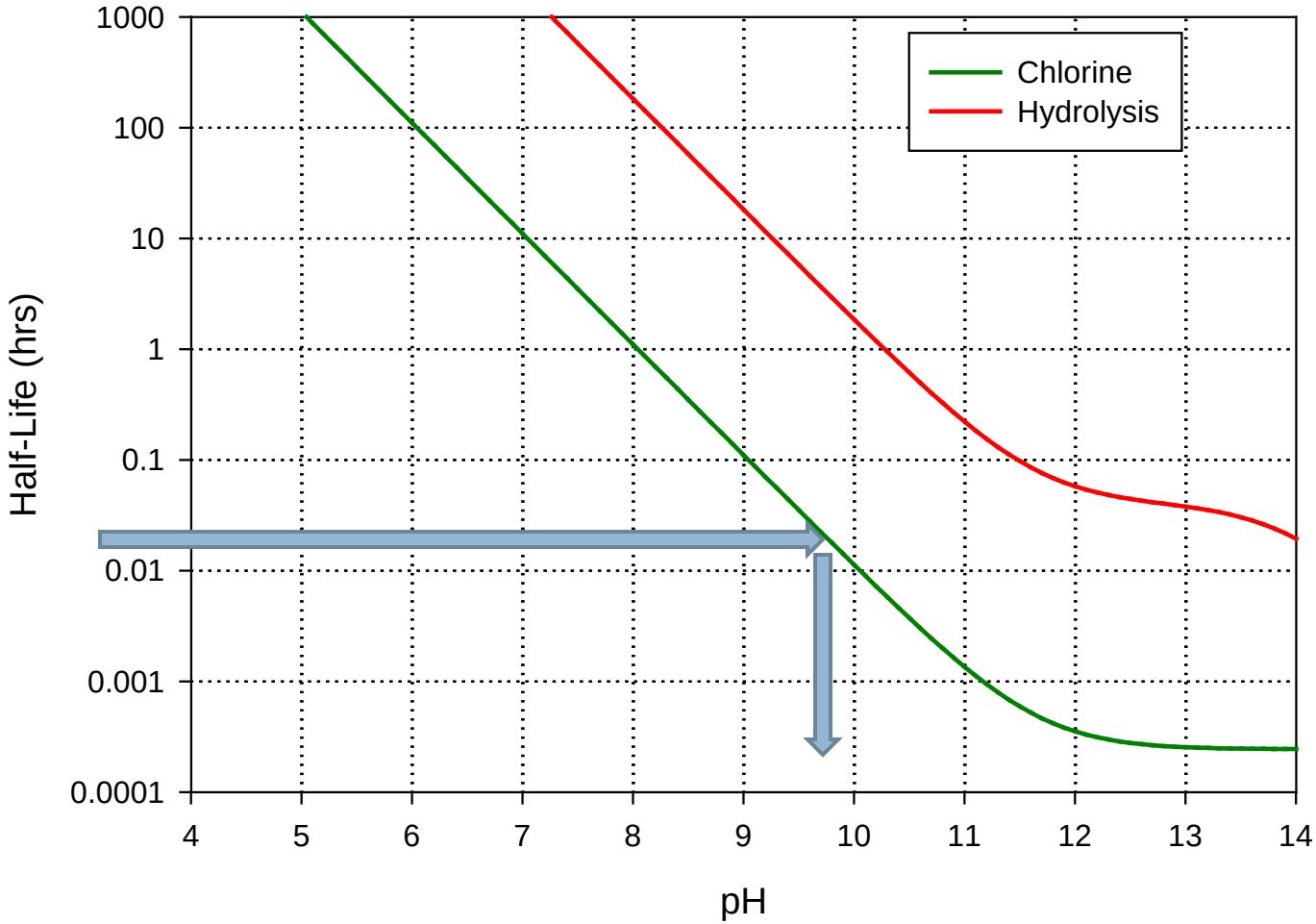


Lab 2

- 2nd order plot



Guthrie model



- To next lecture