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CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #20

Chloramines revisited: bromine, lead and bacteria

Primary Literature

David A. Reckhow

Case Studies

Model Equations 1a

Vikesland, P. J., K. Ozekin, et al. (2001). "Monochloramine decay in model and distribution system waters." Water Research **35(7): 1766-1776.**

#	Reaction	Rate coefficient/equilibrium constant (25°C)	References
1	$HOCl+NH_3 \rightarrow NH_2Cl+H_2O$	$k_1=1.5\times10^{10}$ M^{-1} h^{-1}	Morris and Isaac (1981)
2	$NH_2Cl+H_2O \rightarrow HOCl+NH_3$	$k_2=7.6\times10^{-2}$ h^{-1}	Morris and Isaac (1981)
3	$HOCl+NH_2Cl \rightarrow NHCl_2+H_2O$	$k_3=1.0\times10^{6}$ M^{-1} h^{-1}	Margerum *et al.* (1978)
4	$NHCl_2+H_2O \rightarrow HOCl+NH_2Cl$	$k_4=2.3\times10^{-3}$ h^{-1}	Margerum *et al.* (1978)
5	$NH_2Cl+NH_2Cl \rightarrow NHCl_2+NH_3$	k_d[a]	Vikesland et al. (2001)
6	$NHCl_2+NH_3 \rightarrow NH_2Cl+NH_2Cl$	$k_6=2.2\times10^{8}$ M^{-2} h^{-1}	Hand and Margerum (1983)
7	$NHCl_2+H_2O \rightarrow I$	$k_7=4.0\times10^{5}$ M^{-1} h^{-1}	Jafvert and Valentine (1987)
8	$I+NHCl_2 \rightarrow HOCl+products$	$k_8=1.0\times10^{8}$ M^{-1} h^{-1}	Leao (1981)
9	$I+NH_2Cl \rightarrow products$	$k_9=3.0\times10^{7}$ M^{-1} h^{-1}	Leao (1981)
10	$NH_2Cl+NHCl_2 \rightarrow products$	$k_{10}=55.0$ M^{-1} h^{-1}	Leao (1981)
11	$HOCl \rightarrow H^+ + OCl^-$	$pK_a=7.5$	Snoeyink and Jenkins (1980)
12	$NH_4^+ \rightarrow NH_3+H^+$	$pK_a=9.3$	Snoeyink and Jenkins (1980)
13	$H_2CO_3 \rightarrow HCO_3^-+H^+$	$pK_a=6.3$	Snoeyink and Jenkins (1980)
14	$HCO_3^- \rightarrow CO_3^{2-}+H^+$	$pK_a=10.3$	Snoeyink and Jenkins (1980)

What is "I"

3

- NOH first suggested as a key intermediate by Morris, Weil & Culver (1951)?
  - 12th International Congress of Pure and Applied Chemistry: Abstracts of Papers, New York, Sept 10-13, 1951
- Wei (1972) also proposes NOH
  - Wei, Irvine Wen-Tung. "CHLORINE-AMMONIA BREAKPOINT REACTIONS: KINETICS AND MECHANISM." PhD Harvard University; Advisor: J.C. Morris
  - Acknowledged by Leao (1981)
- Valentine, Jafvert & Leung (1988) say it may or may not be NOH
- Leung & Valentine (1994a, b) say it contains N and Cl
- Maybe it is really several compounds

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Includes: Leao & Selleck (1983); Zhang & Lin, 2013

Model Equations 1b

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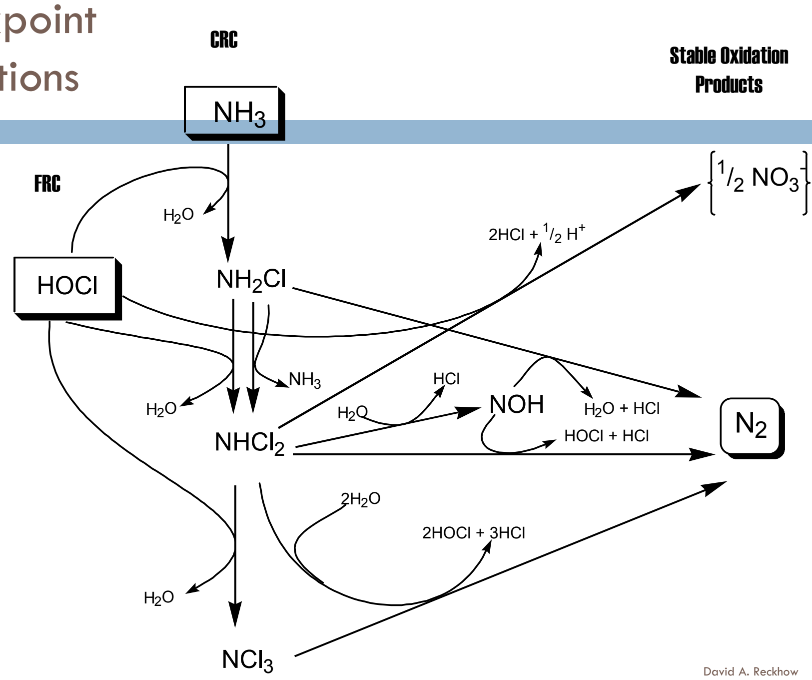
#	Reaction	Rate coefficient/equilibrium constant (25°C)	References
1	$HOCl+NH_3 \rightarrow NH_2Cl+H_2O$	$k_1=1.5\times10^{10}$ M^{-1} h^{-1}	Morris and Isaac (1981)
2	$NH_2Cl+H_2O \rightarrow HOCl+NH_3$	$k_2=7.6\times10^{-2}$ h^{-1}	Morris and Isaac (1981)
3	$HOCl+NH_2Cl \rightarrow NHCl_2+H_2O$	$k_3=1.0\times10^{6}$ M^{-1} h^{-1}	Margerum *et al.* (1978)
4	$NHCl_2+H_2O \rightarrow HOCl+NH_2Cl$	$k_4=2.3\times10^{-3}$ h^{-1}	Margerum *et al.* (1978)
5	$NH_2Cl+NH_2Cl \rightarrow NHCl_2+NH_3$	k_d[a]	Vikesland et al. (2001)
6	$NHCl_2+NH_3 \rightarrow NH_2Cl+NH_2Cl$	$k_6=2.2\times10^{8}$ M^{-2} h^{-1}	Hand and Margerum (1983)
7	$NHCl_2+OH^- \rightarrow NOH+H^++Cl^-$	$k_7=5.5\times10^{5}$ M^{-1} h^{-1}	Leao & Selleck (1983)
8	$NOH+NHCl_2 \rightarrow HOCl+N_2+Cl^-+H^+$	$k_8=1.0\times10^{8}$ M^{-1} h^{-1}	Leao (1981)
9	$NOH+NH_2Cl \rightarrow H_2O+N_2+Cl^-+H^+$	$k_9=3.0\times10^{7}$ M^{-1} h^{-1}	Leao (1981)
10	$NH_2Cl+NHCl_2 \rightarrow N_2+3Cl^-+3H^+$	$k_{10}=55.0$ M^{-1} h^{-1}	Leao (1981)
11	$HOCl \rightarrow H^++OCl^-$	$pK_a=7.5$	Snoeyink and Jenkins (1980)
12	$NH_4^+ \rightarrow NH_3+H^+$	$pK_a=9.3$	Snoeyink and Jenkins (1980)
13	$H_2CO_3 \rightarrow HCO_3^-+H^+$	$pK_a=6.3$	Snoeyink and Jenkins (1980)
14	$HCO_3^- \rightarrow CO_3^{2-}+H^+$	$pK_a=10.3$	Snoeyink and Jenkins (1980)

Breakpoint Reactions

5



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Additional Bromide reactions

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#	Reaction	Rate coefficient/equilibrium constant (25°C)	References
15	$NH_2Cl+H^+ \leftrightarrow NH_3Cl^+$	K = 28 M^{-1}	Gray et al., 1978
15f	$NH_2Cl+H^+ \rightarrow NH_3Cl^+$	k_f = 2.16 × 10^8 M^{-1} h^{-1}	Bousher et al., 1989
15b	$NH_3Cl^+ \rightarrow NH_2Cl+H^+$	k_b = 7.71× 10^6 h^{-1}	
16	$NH_3Cl^++Br^- \rightarrow NH_3Br^++Cl^-$	k_{Br} = 1.8 × 10^8 $M^{-1}h^{-1}$[a]	Trofe et al., 1980
17	$NH_2Cl+NH_3Br^+ \rightarrow NHBrCl+NH_4^+$	k_{fast}	Valentine et al., 1998
18	$HOCl+Br^- \rightarrow HOBr+Cl^-$	k_{HOCl} = 4.8 × 10^6 $M^{-1}h^{-1}$[b]	Kumar & Margerum, 1987
19	$HOBr+NH_2Cl \rightarrow NHBrCl+H_2O$	k_{fast}	Valentine et al., 1998
20	$NHBrCl+H_2O \rightarrow NOH+2H^++Br^-+Cl^-$	k_{20} = 7.2 × 10^5 $M^{-1}h^{-1}$	Zhang & Lin, 2013
21	$NOH+NHBrCl \rightarrow HOBr+N_2+H^++Cl^-$	k_{21} = 5.0 × 10^8 $M^{-1}h^{-1}$	Zhang & Lin, 2013
22	$NHBrCl+NH_2Cl \rightarrow N_2+3H^++2Cl^-+Br^-$	k_{fast}	Valentine et al., 1998

[a]Values were later adjusted by Zhang & Lin to match results; [b]Reaction#18 only includes neutral reaction

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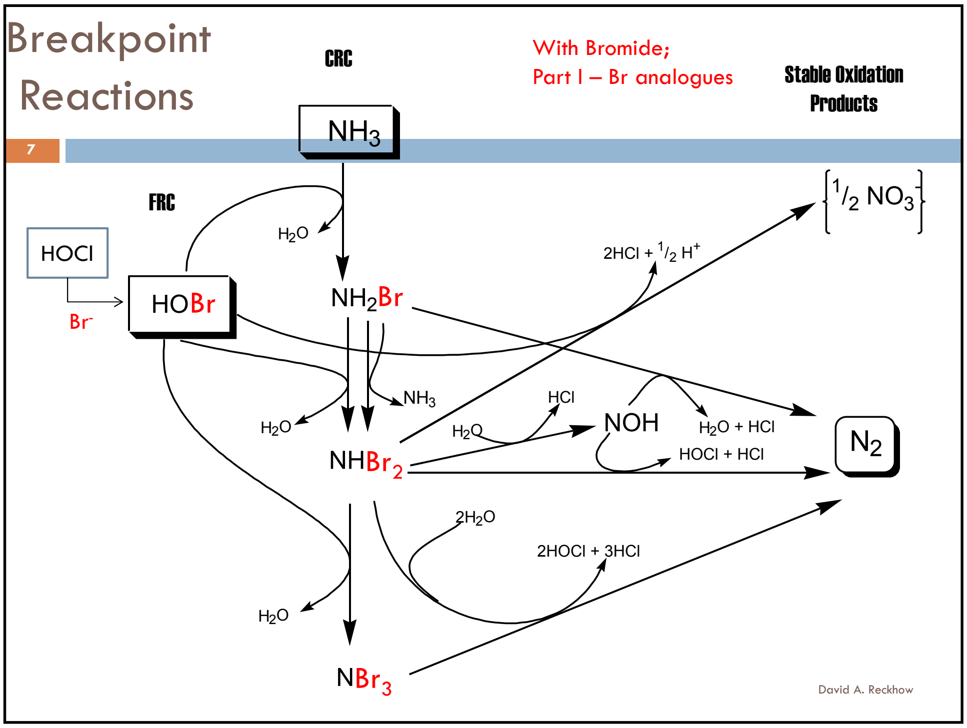
Breakpoint Reactions
7
CRC
With Bromide;
Part I – Br analogues
Stable Oxidation Products
NH3
FRC
HOCl
Br-
HOBr
H2O
NH2Br
NH3
H2O
NHBr2
H2O
NBr3
2HCl + 1/2 H+
1/2 NO3-
HCl
H2O
NOH
H2O + HCl
HOCl + HCl
N2
2H2O
2HOCl + 3HCl
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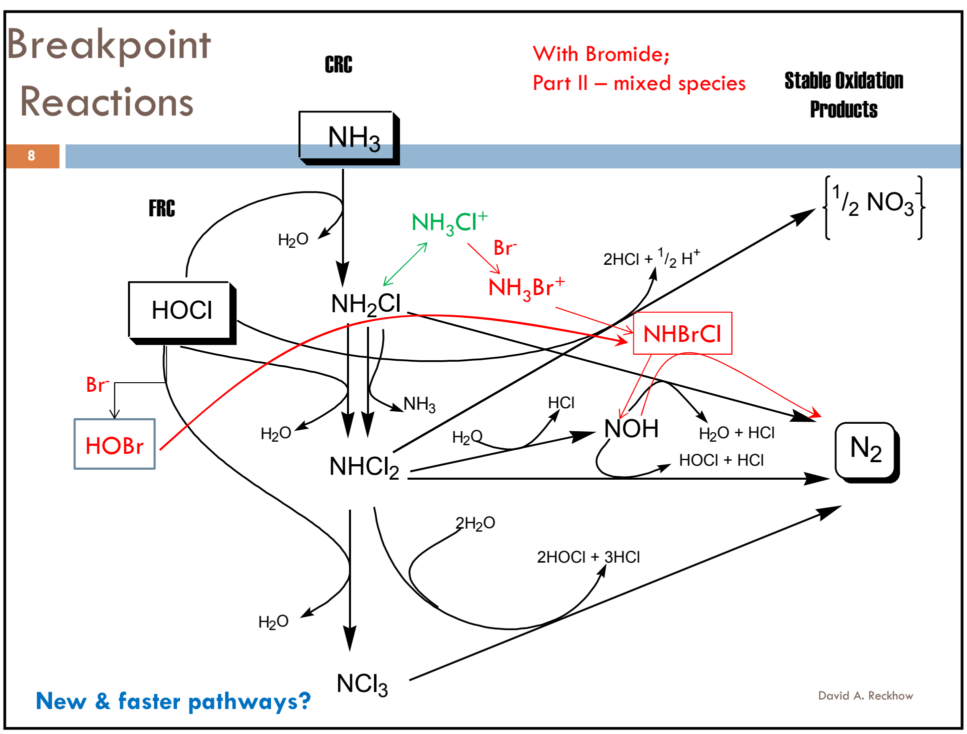
Breakpoint Reactions
8
CRC
With Bromide;
Part II – mixed species
Stable Oxidation Products
NH3
FRC
H2O
NH3Cl+
Br-
NH3Br+
NH2Cl
HOCl
NHBrCl
Br-
HOBr
NH3
H2O
NHCl2
2HCl + 1/2 H+
1/2 NO3-
HCl
H2O
NOH
H2O + HCl
HOCl + HCl
N2
2H2O
2HOCl + 3HCl
H2O
NCl3
New & faster pathways?
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Chloramines: simplified

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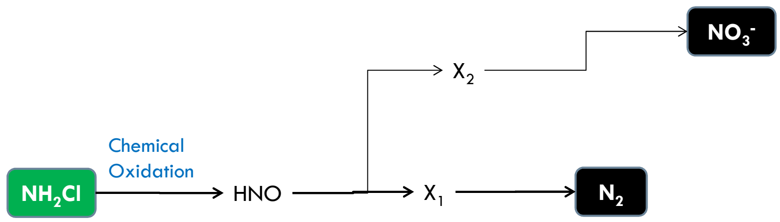
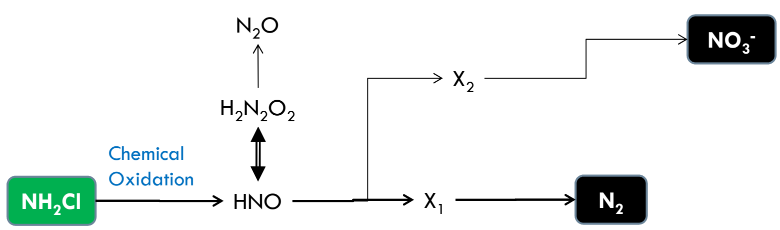


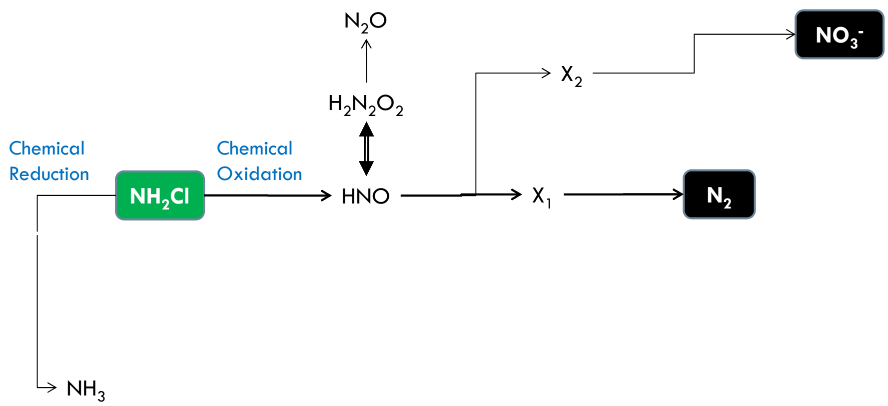
Chloramines: with nitroxyl

10



Chloramines: with chlorine demand

11



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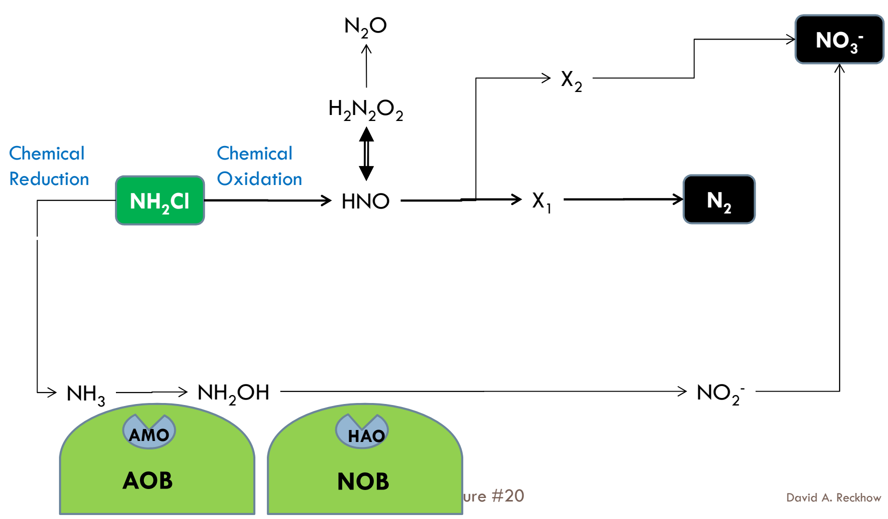
Chloramines: with nitrification

12



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Chloramines: the larger picture

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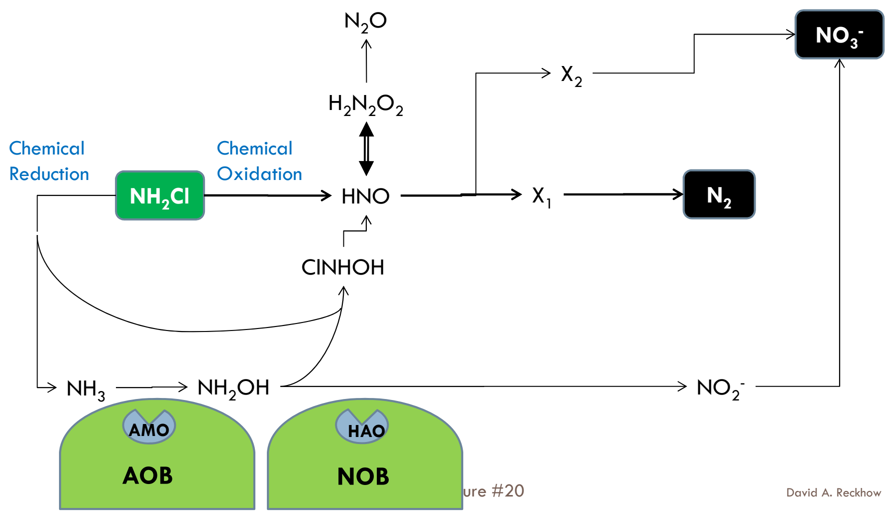

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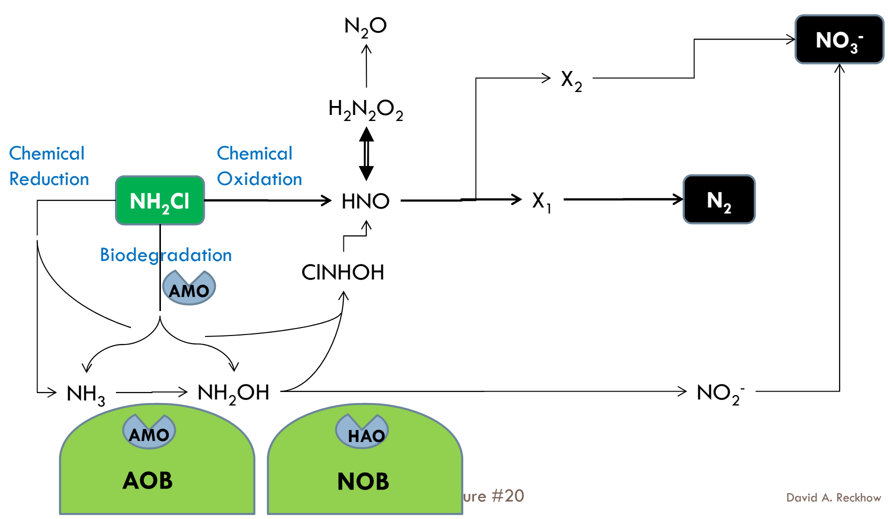
Chloramines: with cometabolism

14



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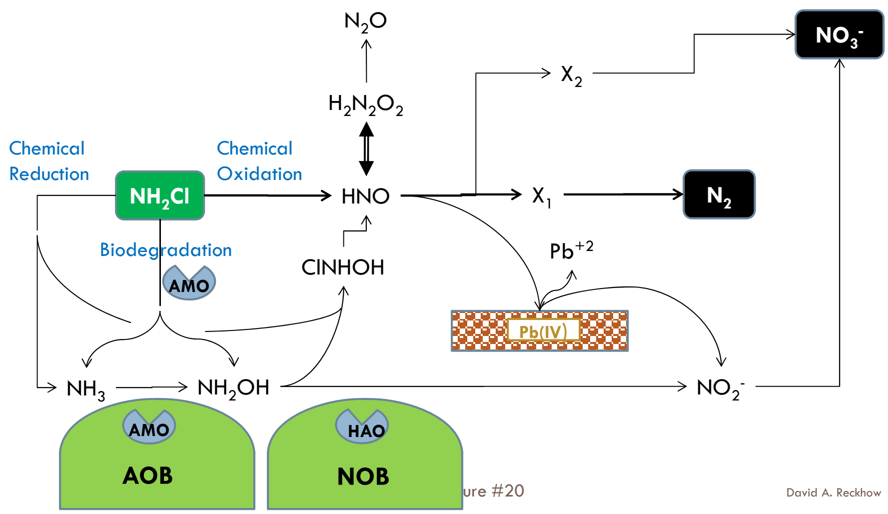
Chloramines: with pipe reactions

15



Lead and Nitrite reactions

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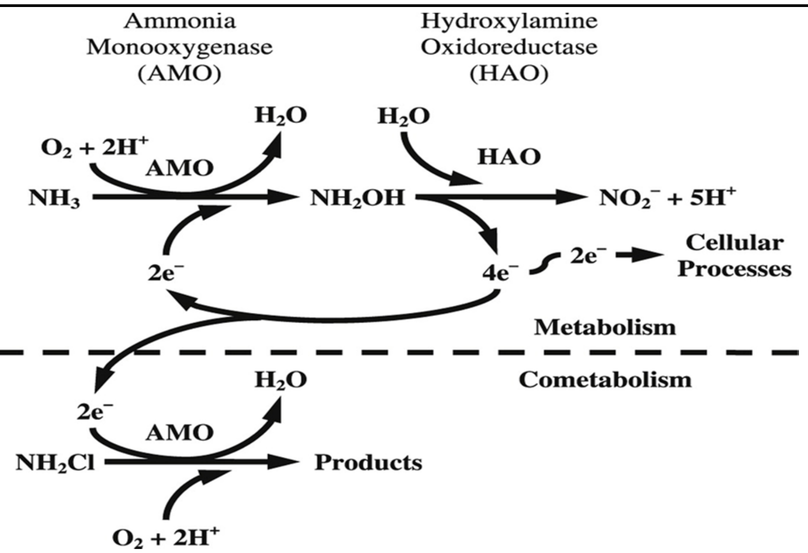
#	Reaction	Rate coefficient/equilibrium constant (25°C)	References
23	$NOH+PbO_2 \leftrightarrow Pb^{+2}+NO_2^-+OH^-$	k_{23} = 1.3 x 10^5 m^{-2}h^{-1}	Zhang & Lin, 2013
24	$NO_2^-+NH_2Cl+H_2O \rightarrow NO_3^- +NH_3Cl+H^++Cl^-$	k_{24} = 4.0 × 10^7 M^{-1}h^{-1}	Zhang & Lin, 2013
25	$NO_2^-+NHCl_2+2H_2O \rightarrow NO_3^- +HOCl+NH_3+H^++Cl^-$	k_{25} = 2.0 × 10^8 M^{-1}h^{-1}	Zhang & Lin, 2013
26	$NO_2^-+NHBrCl+2H_2O \rightarrow NO_3^- +HOBr+NH_3+H^++Cl^-$	k_{26} = 9.0 × 10^8 M^{-1}h^{-1}	Zhang & Lin, 2013

Zhang, Y. Y. and Y. P. Lin (2013). "Release of Pb(II) from the reduction of Pb(IV) corrosion product PbO2 induced by bromide-catalyzed monochloramine decomposition." Environmental Science & Technology **47: 10931-10938.**



Monochloramine cometabolism by Nitrosomonas europaea under drinking water conditions

Maestre, J. P., D. G. Wahman, et al. (2013). "Monochloramine cometabolism by Nitrosomonas europaea under drinking water conditions." Water Research **47(13): 4701-4709.**

Cometabolic Model I

Table 2 – Process matrix for batch kinetic experiments.

Kinetic rate	Kinetic rate expression	Reaction stoichiometry				
		S_{TOTNH_3}	S_{NH_2Cl}	X_a	S_{NO_2}	S_{UAP}
Ammonia first-order	$k_{1TOTNH_3} X_a S_{TOTNH_3} \alpha_1$	−1			1	f_{UAP}
Ammonia monod	$\frac{k_{TOTNH_3} X_a S_{TOTNH_3} \alpha_1}{K_{S_{NH_3-N}} + S_{TOTNH_3} \alpha_1}$	−1			1	f_{UAP}
First-order cometabolism	$k_{1NH_2Cl} X_a S_{NH_2Cl}$		−1		1	
First-order-reductant cometabolism	$k_{1NH_2Cl} X_a S_{NH_2Cl} \left(\frac{S_{TOTNH_3} \alpha_1}{K_{S_{NH_3-N}} S_{TOTNH_3} \alpha_1} \right)$ +		−1		1	
Biomass reactivity	$k_{Biomass} X S_{NH_2Cl}$	1	−1			
Biomass inactivation	$k_{Inact} X_a S_{NH_2Cl}$			−1		
UAP Reactivity	$k_{UAP} S_{UAP} S_{NH_2Cl}$	1	−1			−1

f_{UAP} – UAP formation fraction from $TOTNH_3$ degradation, moles UAP formed/moles $TOTNH_3$ degraded.
k_{1TOTNH_3} – ammonia first-order rate constant, moles $TOTNH_3$-L/(moles NH_3–N mg TSS day).
X_a – active biomass concentration, mg TSS/L.
S_{TOTNH_3} – $TOTNH_3$ concentration, moles $TOTNH_3$/L.
α_1 – NH_3–N fraction of $TOTNH_3$.
k_{TOTNH_3} – ammonia maximum specific rate of degradation, moles $TOTNH_3$/mg TSS-day.
$K_{S_{NH_3-N}}$ – ammonia half-saturation constant, moles NH_3–N/L.
k_{1NH_2Cl} – monochloramine first-order cometabolism rate constant, L/mg TSS-day.
S_{NH_2Cl} – monochloramine concentration, moles Cl_2/L.
$k_{Biomass}$ – monochloramine reaction with biomass rate constant, L/mg TSS-day.
X – initial biomass concentration, mg TSS/L.
k_{Inact} – active biomass inactivation rate constant, L/moles Cl_2-day.
k_{UAP} – monochloramine reaction rate constant with UAP, L/moles UAP-day.
S_{UAP} – UAP concentration, moles UAP/L.

Maestre, J. P., D. G. Wahman, et al. (2013). "Monochloramine cometabolism by Nitrosomonas europaea under drinking water conditions." Water Research **47(13): 4701-4709.**

Cometabolic Model II

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Table 3 – Summary and comparison of kinetic parameters for *N. europaea*.

Parameter	Description	Units	Estimate	Standard deviation
k_{TOTNH_3}	Ammonia maximum specific rate of degradation	mg $TOTNH_3$/mg TSS–day	2.9	Fixed constant
$k_{S_{NH_3-N}}$	Ammonia half-saturation constant	mg NH_3–N/L	0.13	0.0035
k_{1TOTNH_3}	Ammonia first-order rate constant	$\frac{(\text{mg TOTNH}_3)(\text{L})}{(\text{mg NH}_3-\text{N})(\text{mg TSS})(\text{day})}$	22.3	0.6
$k^{*}_{1TOTNH_3}\alpha 1_{pH8.3}$	Ammonia first-order rate constant at pH 8.3	L/mg TSS–day	2.3	0.06
$k_{Biomass}$	Monochloramine reaction with biomass rate constant	L/mg TSS–day	0.18	0.031
k_{Inact}	Active biomass inactivation rate constant	L/mg Cl_2–day	224	22
f_{UAP}	UAP formation fraction from $TOTNH_3$ metabolism	mole UAP/mole $TOTNH_3$	0.029	0.0091
k_{UAP}	Monochloramine reaction rate constant with UAP	1/M-day – L/moles UAP-day	1.85×10^7	1.54×10^7
k_{1NH_2Cl}	Monochloramine first-order cometabolism rate constant	L/mg TSS–day	2.1	0.53
k_{1TCM} [a]	Chloroform first-order cometabolism rate constant	L/mg TSS–day	0.10	
k_{1TBM} [a]	Bromoform first-order cometabolism rate constant	L/mg TSS–day	0.23	

a Chloroform and bromoform rate constants from Wahman et al. (2005).

Maestre, J. P., D. G. Wahman, et al. (2013). "Monochloramine cometabolism by Nitrosomonas europaea under drinking water conditions." Water Research **47(13): 4701-4709.**

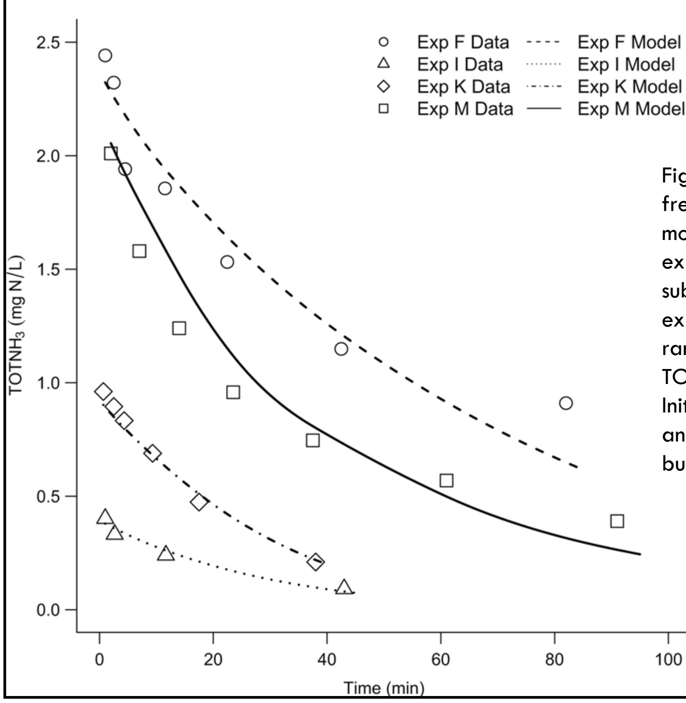

Fig. 1. Comparison of total free ammonia ($TOTNH_3$) model simulations and experimental data for a subset of positive control experiments shown over a range of initial $TOTNH_3$ concentrations. Initial conditions: pH 8.3 and 4 mM bicarbonate buffer.

Maestre, J. P., D. G. Wahman, et al. (2013). "Monochloramine cometabolism by Nitrosomonas europaea under drinking water conditions." Water Research **47(13): 4701-4709.**

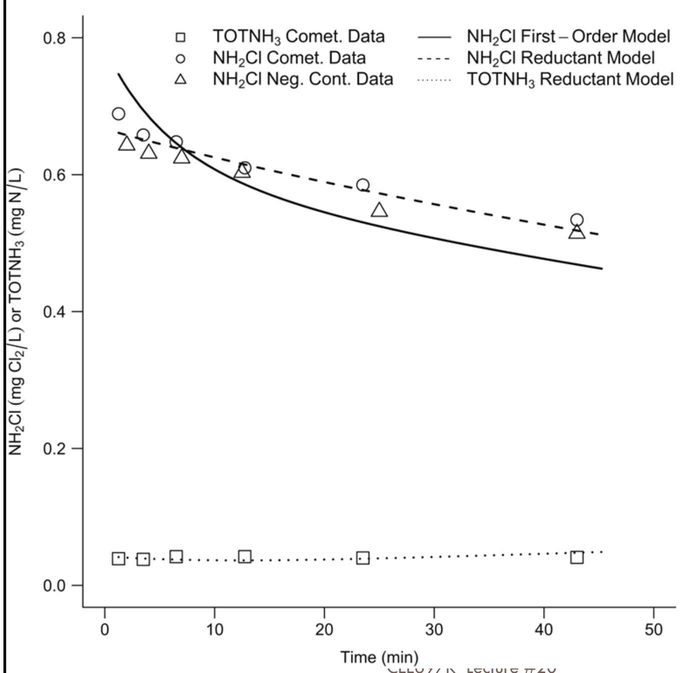

Fig. 2. Comparison of monochloramine (NH_2Cl) and total free ammonia ($TOTNH_3$) model simulations and experimental data in Experiment J. Comet. = Cometabolism and Neg. Cont. = Negative Control. Initial conditions: pH 8.3, 4 mM bicarbonate buffer, and 5:1 Cl_2:N mass ratio.

Maestre, J. P., D. G. Wahman, et al. (2013). "Monochloramine cometabolism by Nitrosomonas europaea under drinking water conditions." Water Research 47(13): 4701-4709.

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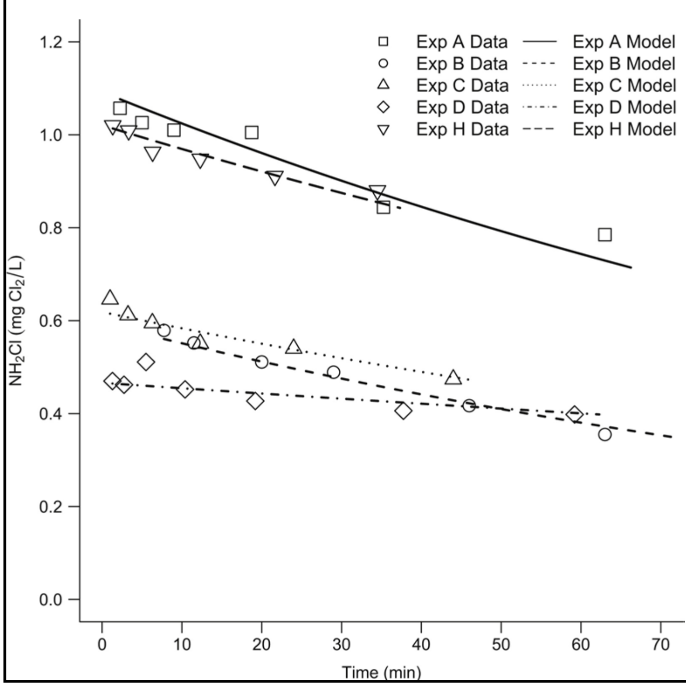

Fig. 3. Comparison of monochloramine (NH_2Cl) model simulations and experimental data for a subset of negative control experiments for a range of initial NH_2Cl concentrations. Experiments detail the reaction of NH_2Cl with chlorobenzene inactivated biomass. Initial conditions: pH 8.3 and 4 mM bicarbonate buffer.

Maestre, J. P., D. G. Wahman, et al. (2013). "Monochloramine cometabolism by Nitrosomonas europaea under drinking water conditions." Water Research 47(13): 4701-4709.

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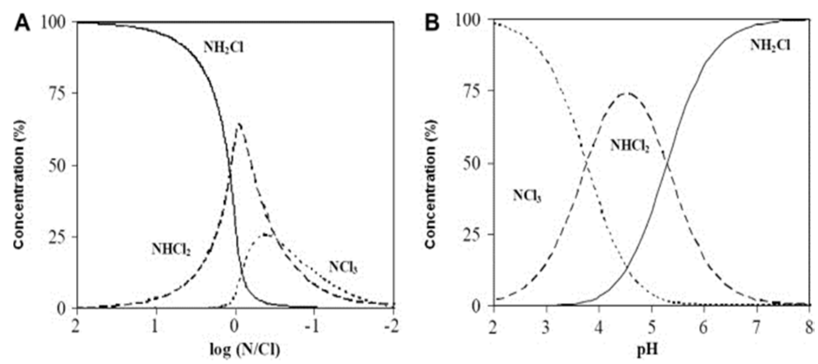

Figure 1 Distribution of inorganic chloramines depending on (A) molar ratio N/Cl, and on (B) pH, according to Cimetière <ce:cross-ref refid="b0025"> [5]</ce:cross-ref> .

Said Kinani , Bertille Richard , Yasmine Souissi , Stéphane Bouchonnet

Analysis of inorganic chloramines in water

TrAC Trends in Analytical Chemistry Volume 33 2012 55 - 67

http://dx.doi.org/10.1016/j.trac.2011.10.006

Vikesland modification

- Modified version of equation #5 for carbonate
  - $k_d = k_{H}^{+}[H^+] + k_{H2CO3}[H_2CO_3] + k_{HCO3}[HCO_3]$
  - Where
    - $k_H^+ = 2.5 \times 10^7\ M^{-2}h^{-1}$
    - $k_{H2CO3} = 4 \times 10^4\ M^{-2}h^{-1}$
    - $k_{HCO3} = 800\ M^{-2}h^{-1}$
    - I is the unidentified monochloramine auto-decomposition intermediate

Vikesland, P. J., K. Ozekin, et al. (2001). "Monochloramine decay in model and distribution system waters." Water Research **35(7): 1766-1776.**

Temperature Effects

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Reaction	Rate coefficient/equilibrium constant	References
$HOCl+NH_3 \rightarrow NH_2Cl+H_2O$	$k_{1.1}=2.37\times10^{12}\exp(-1510/T)\ M^{-1}\ h^{-1}$	Morris and Isaac (1981)
$NH_2Cl+H_2O \rightarrow HOCl+NH_3$	$k_{1.2}=6.7\times10^{11}\exp(-8800/T)\ h^{-1}$	Morris and Isaac (1981)
$HOCl+NH_2Cl \rightarrow NHCl_2+H_2O$	$k_{1.3}=1.08\times10^{9}\exp(-2010/T)\ M^{-1}\ h^{-1}$	Margerum*et al.*(1978)
$NH_2Cl+NH_2Cl \rightarrow NHCl_2+NH_3$	$k_{1.5}=kH^{+}[H^{+}]+kHCO_3[HCO_3^{-}]+kH_2CO_3[H_2CO_3]$	
	$k_{H+}=3.78\times10^{10}\exp(-2169/T)\ M^{-2}\ h^{-1}$	Granstrom (1954)
	$k_{HCO3}=1.5\times10^{35}\exp(-22144/T)\ M^{-2}\ h^{-1}$	Vikesland et al. (2001)
	$k_{H2CO3}=2.95\times10^{10}\exp(-4026/T)\ M^{-2}\ h^{-1}$	Vikesland et al. (2001)
$H_2CO_3 \rightleftharpoons HCO_3^{-}+H^{+}$	$pka=1.48\times10^{-4}(T)^2-9.39\times10^{-2}(T)+21.2$	Snoeyink and Jenkins (1980)
$HCO_3^{-} \rightleftharpoons H^{+}+CO_3^{2-}$	$pka=1.19\times10^{-4}(T)^2-7.99\times10^{-2}(T)+23.6$	Snoeyink and Jenkins (1980)
$NH_4^{+} \rightleftharpoons NH_3+H^{+}$	$pka=1.03\times10^{-4}(T)^2-9.21\times10^{-2}(T)+27.6$	Bates and Pinching (1950)
$HOCl \rightleftharpoons OCl^{-}+H^{+}$	$pk_a=1.18\times10^{-4}(T)^2-7.86\times10^{-2}(T)+20.5$	

ACS Publications
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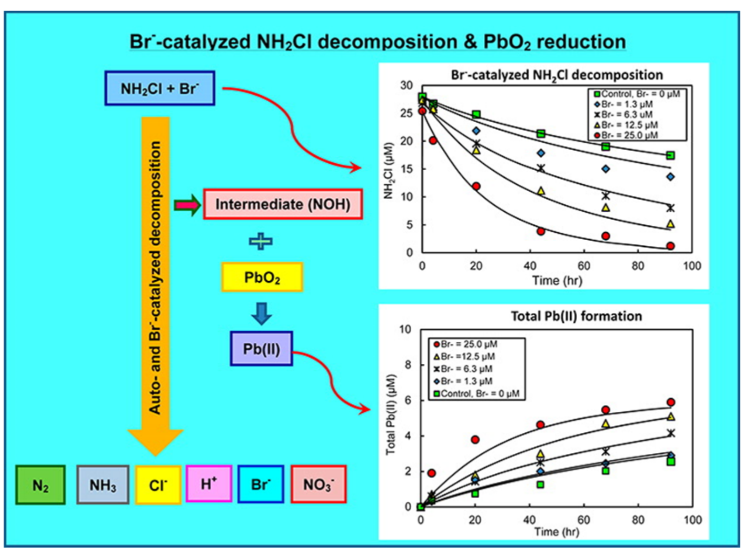

Zhang, Y. Y. and Y. P. Lin (2013). "Release of Pb(II) from the reduction of Pb(IV) corrosion product PbO2 induced by bromide-catalyzed monochloramine decomposition." Environmental Science & Technology **47: 10931-10938.**

- To next lecture