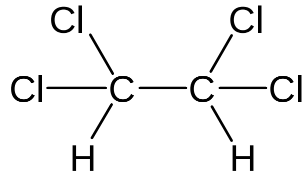
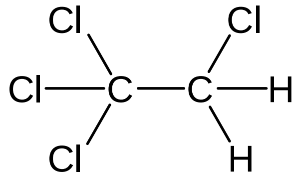
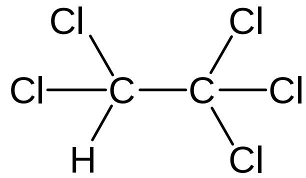
EXAMPLE

Hydrolysis of Chlorinated Ethanes



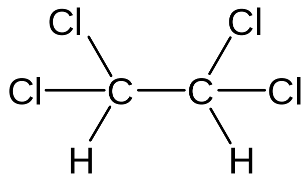


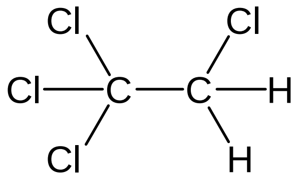


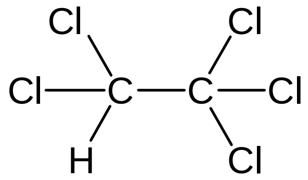
- Assume that the three polychlorinated ethanes,
  1,1,2,2-tetrachloroethane,
  1,1,1,2-tetrachloroethane, and
  pentachloroethane
  are introduced into a lake by accident.
  Calculate the half-life for chemical transformation of the three compounds in
  (a) the **epilimnion** of the lake (*T* = 25°C, pH 8.5) and
  (b) the **hypolimnion** of the lake (*T* = 5°C, pH 7.5).
  Furthermore, indicate the pH of the I_{NB} for the epilimnion and hypolimnion.
  (c) What is (are) the transformation product(s) of these compounds? Explain the different reactivities of the three compounds.

Hydrolysis of Chlorinated Ethanes

- Which compound will hydrolyze fastest?

A. 

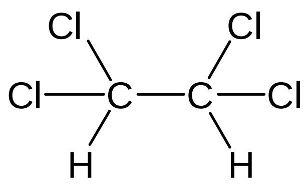
B. 

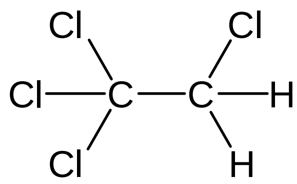
C. 

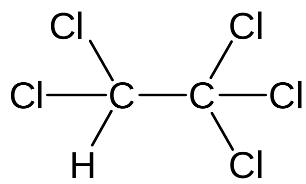
Hydrolysis of Chlorinated Ethanes

- Data

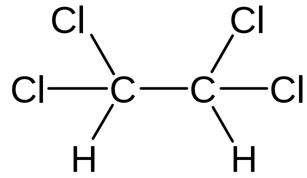
compound	neutral k_N, 25°C (s^{-1})	neutral E_a ($kJ\ mol^{-1}$)	base-catalyzed k_B, 25°C ($M^{-1}\ s^{-1}$)	base-catalyzed E_a ($kJ\ mol^{-1}$)
1,1,2,2-tetrachloroethane	$<1\times10^{-10}$	93	5×10^{-1}	78
1,1,1,2-tetrachloroethane	4×10^{-10}	95	3.5×10^{-4}	100
pentachloroethane	8×10^{-10}	95	2.7×10^{1}	80

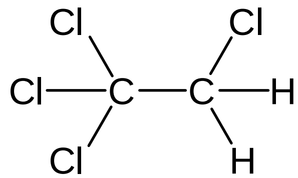


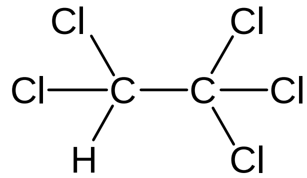




Hydrolysis of Chlorinated Ethanes







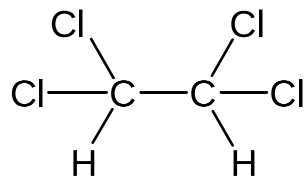
- Temperature correction
  - T_1 = 25 °C = 298.15 K
    T_2 = 5 °C = 278.15 K

$$k_{T_2} = k_{T_1} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

  - E_a is activation energy (J mol^{-1})

Hydrolysis of Chlorinated Ethanes

- Temperature correction for 1,1,2,2-tca



  - T_1 = 25 °C = 298.15 K; T_2 = 5 °C = 278.15 K
    E_a = 93,000 J mol^{-1}; R = 8.314 J mol^{-1} K^{-1}
    $k_{T1} = k_N$ (25 °C) = 1×10^{-10} s^{-1}

$$k_{T_2} = k_{T_1} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$$

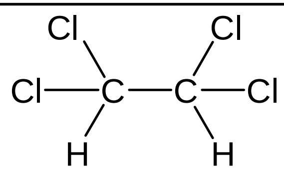
$$k_N\left(5\,^\circ\mathrm{C}\right) = \left(1.0\times10^{-10}\ \mathrm{s}^{-1}\right)\exp\left[-\frac{93,000\ \mathrm{J\,mol^{-1}}}{8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}}\left(\frac{1}{278.15\,\mathrm{K}}-\frac{1}{298.15\,\mathrm{K}}\right)\right]$$

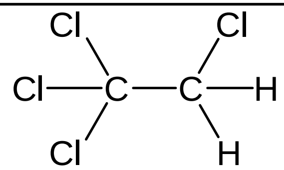
$$k_N\left(5\,^\circ\mathrm{C}\right) = 6.7\times10^{-12}\ \mathrm{s}^{-1}$$

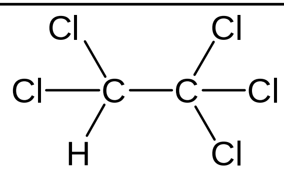
Hydrolysis of Chlorinated Ethanes

- Temperature correction and calculations

		1,1,2,2-tetrachloro-	1,1,1,2-tetrachloro-	pentachloro-
epilimnion	k_N (s^{-1})	$1x10^{-10}$	$4x10^{-10}$	$8x10^{-10}$
25 °C	k_B (M^{-1} s^{-1})	$5x10^{-1}$	$3.5x10^{-4}$	$2.7x10^{1}$
pH 8.5	k_B [OH^-] (s^{-1})	$1.6x10^{-6}$	$1.1x10^{-9}$	$8.5x10^{-5}$
[OH^-] = $10^{-5.5}$ M	k_h (s^{-1})	$1.6x10^{-6}$	$1.5x10^{-9}$	$8.5x10^{-5}$
K_w = $10^{-14.00}$	$t_{1/2}$ (s)	$4.3x10^{5}$	$4.6x10^{8}$	8,200
	$t_{1/2}$ (d)	5.0	5,300	0.094
	I_{NB}	4.3	8.1	3.5
hypolimnion	k_N (s^{-1})	$6.7x10^{-12}$	$2.5x10^{-11}$	$5.1x10^{-11}$
5 °C	k_B (M^{-1} s^{-1})	$5.2x10^{-2}$	$1.9x10^{-5}$	$2.7x10^{0}$
pH 7.5	k_B [OH^-] (s^{-1})	$3.0x10^{-9}$	$1.1x10^{-12}$	$1.6x10^{-7}$
[OH^-] = $10^{-7.23}$ M	k_h (s^{-1})	$3.0x10^{-9}$	$2.6x10^{-11}$	$1.6x10^{-7}$
K_w = $10^{-14.73}$	$t_{1/2}$ (s)	$2.3x10^{8}$	$2.7x10^{10}$	$4.3x10^{6}$
	$t_{1/2}$ (d)	2,700	310,000	50
	I_{NB}	5.0	8.8	4.0

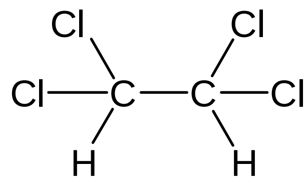






Hydrolysis of Chlorinated Ethanes

- Temperature correction for 1,1,2,2-tca
  - T_1 = 25 °C = 298.15 K; T_2 = 5 °C = 278.15 K
    E_a = 78,000 J mol^{-1}; R = 8.314 J mol^{-1} K^{-1}
    $k_{T1} = k_B$ (25 °C) = 5×10^{-1} M^{-1} s^{-1}



$$k_{T_2} = k_{T_1} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$$

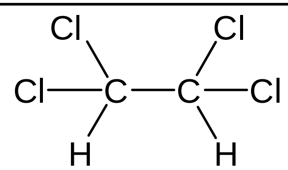
$$k_B\left(5\,\mathrm{C}\right) = \left(5\times10^{-1}\ \mathrm{s}^{-1}\right)\exp\left[-\frac{78,000\,\mathrm{J\,mol}^{-1}}{8.314\,\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}}\left(\frac{1}{278.15\,\mathrm{K}}-\frac{1}{298.15\,\mathrm{K}}\right)\right]$$

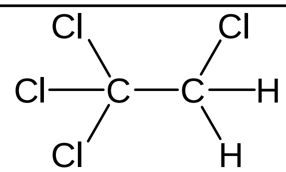
$$k_B\left(5\,\mathrm{C}\right) = 5.2\times10^{-2}\ \mathrm{s}^{-1}$$

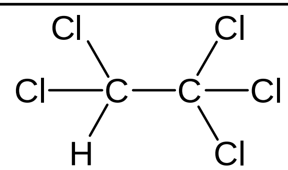
Hydrolysis of Chlorinated Ethanes

- Temperature correction and calculations

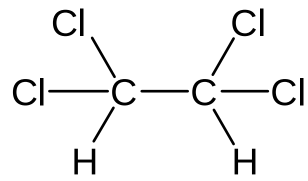
		1,1,2,2-tetrachloro-	1,1,1,2-tetrachloro-	pentachloro-
epilimnion	k_N (s^{-1})	$1x10^{-10}$	$4x10^{-10}$	$8x10^{-10}$
25 C	k_B (M^{-1} s^{-1})	$5x10^{-1}$	$3.5x10^{-4}$	$2.7x10^{1}$
pH 8.5	k_B [OH^-] (s^{-1})	$1.6x10^{-6}$	$1.1x10^{-9}$	$8.5x10^{-5}$
[OH^-] = $10^{-5.5}$ M	k_h (s^{-1})	$1.6x10^{-6}$	$1.5x10^{-9}$	$8.5x10^{-5}$
K_w = $10^{-14.00}$	$t_{1/2}$ (s)	$4.3x10^{5}$	$4.6x10^{8}$	8,200
	$t_{1/2}$ (d)	5.0	5,300	0.094
	I_{NB}	4.3	8.1	3.5
hypolimnion	k_N (s^{-1})	$6.7x10^{-12}$	$2.5x10^{-11}$	$5.1x10^{-11}$
5 C	k_B (M^{-1} s^{-1})	$5.2x10^{-2}$	$1.9x10^{-5}$	$2.7x10^{0}$
pH 7.5	k_B [OH^-] (s^{-1})	$3.0x10^{-9}$	$1.1x10^{-12}$	$1.6x10^{-7}$
[OH^-] = $10^{-7.23}$ M	k_h (s^{-1})	$3.0x10^{-9}$	$2.6x10^{-11}$	$1.6x10^{-7}$
K_w = $10^{-14.73}$	$t_{1/2}$ (s)	$2.3x10^{8}$	$2.7x10^{10}$	$4.3x10^{6}$
	$t_{1/2}$ (d)	2,700	310,000	50
	I_{NB}	5.0	8.8	4.0







Hydrolysis of Chlorinated Ethanes



- $[OH^-]$ at 5 °C and pH 7.5

$$K_w = \left[H^+\right]\left[OH^-\right]$$

$$\left[OH^-\right] = \frac{K_w(5\mathrm{C})}{\left[H^+\right]} = \frac{10^{-14.73}}{10^{-7.5}} = 10^{-7.23}\ \mathrm{M}$$

- First-order base-catalyzed hydrolysis

$$k_{OH} = k_B\left[OH^-\right] = \left(5.2\times10^{-2}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}\right)\left(10^{-7.23}\ \mathrm{M}\right)$$

$$k_{OH} = 3.0\times10^{-9}\ \mathrm{s}^{-1}$$

- overall hydrolysis

$$k_h = k_N + k_B\left[OH^-\right] = k_N + k_{OH}$$

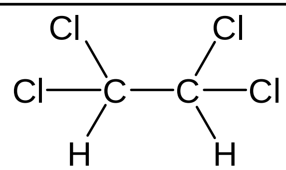
$$k_h = 6.7\times10^{-12}\ \mathrm{s}^{-1} + 3.0\times10^{-9}\ \mathrm{s}^{-1}$$

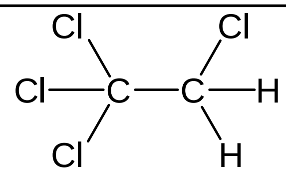
$$k_h = 3.0\times10^{-9}\ \mathrm{s}^{-1}$$

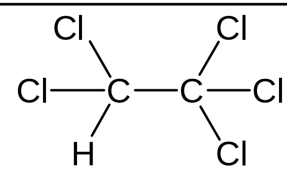
Hydrolysis of Chlorinated Ethanes

- Temperature correction and calculations

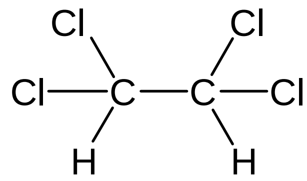
		1,1,2,2-tetrachloro-	1,1,1,2-tetrachloro-	pentachloro-
epilimnion	k_N (s^{-1})	$1x10^{-10}$	$4x10^{-10}$	$8x10^{-10}$
25 C	k_B (M^{-1} s^{-1})	$5x10^{-1}$	$3.5x10^{-4}$	$2.7x10^{1}$
pH 8.5	k_B [OH^-] (s^{-1})	$1.6x10^{-6}$	$1.1x10^{-9}$	$8.5x10^{-5}$
[OH^-] = $10^{-5.5}$ M	k_h (s^{-1})	$1.6x10^{-6}$	$1.5x10^{-9}$	$8.5x10^{-5}$
K_w = $10^{-14.00}$	$t_{1/2}$ (s)	$4.3x10^{5}$	$4.6x10^{8}$	8,200
	$t_{1/2}$ (d)	5.0	5,300	0.094
	I_{NB}	4.3	8.1	3.5
hypolimnion	k_N (s^{-1})	$6.7x10^{-12}$	$2.5x10^{-11}$	$5.1x10^{-11}$
5 C	k_B (M^{-1} s^{-1})	$5.2x10^{-2}$	$1.9x10^{-5}$	$2.7x10^{0}$
pH 7.5	k_B [OH^-] (s^{-1})	$3.0x10^{-9}$	$1.1x10^{-12}$	$1.6x10^{-7}$
[OH^-] = $10^{-7.23}$ M	k_h (s^{-1})	$3.0x10^{-9}$	$2.6x10^{-11}$	$1.6x10^{-7}$
K_w = $10^{-14.73}$	$t_{1/2}$ (s)	$2.3x10^{8}$	$2.7x10^{10}$	$4.3x10^{6}$
	$t_{1/2}$ (d)	2,700	310,000	50
	I_{NB}	5.0	8.8	4.0







Hydrolysis of Chlorinated Ethanes



- Half-life

$$t_{1/2} = \frac{\ln 2}{k_h} = \frac{0.693}{3.0 \times 10^{-9}\ \mathrm{s}^{-1}}$$

$$t_{1/2} = 2.3 \times 10^{8}\ \mathrm{s} = 2{,}700\ \mathrm{d}$$

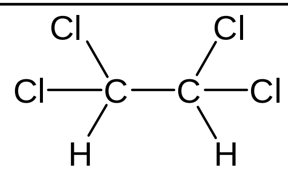
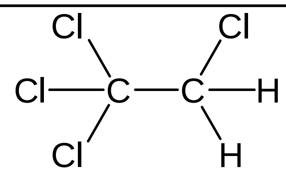
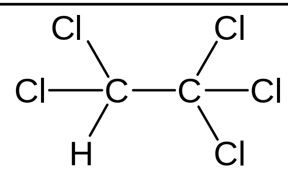
- pH of the I_{NB}

$$I_{NB} = \log\left(\frac{k_N}{k_B K_w}\right) = \log\left(\frac{6.7 \times 10^{-12}\ \mathrm{s}^{-1}}{\left(5.2 \times 10^{-2}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}\right)\left(10^{-14.73}\right)}\right)$$

$$I_{NB} = 5.0$$

Hydrolysis of Chlorinated Ethanes

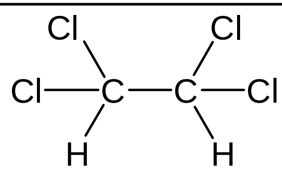
- Temperature correction and calculations

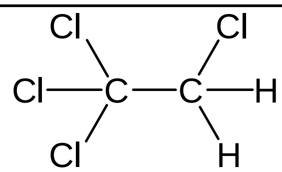
		1,1,2,2-tetrachloro-	1,1,1,2-tetrachloro-	pentachloro-
epilimnion	k_N (s^{-1})	1×10^{-10}	4×10^{-10}	8×10^{-10}
25 C	k_B (M^{-1} s^{-1})	5×10^{-1}	3.5×10^{-4}	2.7×10^{1}
pH 8.5	k_B [OH^-] (s^{-1})	1.6×10^{-6}	1.1×10^{-9}	8.5×10^{-5}
[OH^-] = $10^{-5.5}$ M	k_h (s^{-1})	1.6×10^{-6}	1.5×10^{-9}	8.5×10^{-5}
$K_w = 10^{-14.00}$	$t_{1/2}$ (s)	4.3×10^{5}	4.6×10^{8}	8,200
	$t_{1/2}$ (d)	5.0	5,300	0.094
	I_{NB}	4.3	8.1	3.5
hypolimnion	k_N (s^{-1})	6.7×10^{-12}	2.5×10^{-11}	5.1×10^{-11}
5 C	k_B (M^{-1} s^{-1})	5.2×10^{-2}	1.9×10^{-5}	2.7×10^{0}
pH 7.5	k_B [OH^-] (s^{-1})	3.0×10^{-9}	1.1×10^{-12}	1.6×10^{-7}
[OH^-] = $10^{-7.23}$ M	k_h (s^{-1})	3.0×10^{-9}	2.6×10^{-11}	1.6×10^{-7}
$K_w = 10^{-14.73}$	$t_{1/2}$ (s)	2.3×10^{8}	2.7×10^{10}	4.3×10^{6}
	$t_{1/2}$ (d)	2,700	310,000	50
	I_{NB}	5.0	8.8	4.0
				

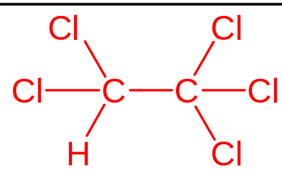
Hydrolysis of Chlorinated Ethanes

- Fastest? greatest k_h, shortest half-life

		1,1,2,2-tetrachloro-	1,1,1,2-tetrachloro-	pentachloro-
epilimnion	k_N (s^{-1})	1×10^{-10}	4×10^{-10}	8×10^{-10}
25 C	k_B ($M^{-1}\ s^{-1}$)	5×10^{-1}	3.5×10^{-4}	2.7×10^{1}
pH 8.5	k_B [OH^-] (s^{-1})	1.6×10^{-6}	1.1×10^{-9}	8.5×10^{-5}
[OH^-] = $10^{-5.5}$ M	k_h (s^{-1})	1.6×10^{-6}	1.5×10^{-9}	8.5×10^{-5}
$K_w = 10^{-14.00}$	$t_{1/2}$ (s)	4.3×10^{5}	4.6×10^{8}	8,200
	$t_{1/2}$ (d)	5.0	5,300	0.094
	I_{NB}	4.3	8.1	3.5
hypolimnion	k_N (s^{-1})	6.7×10^{-12}	2.5×10^{-11}	5.1×10^{-11}
5 C	k_B ($M^{-1}\ s^{-1}$)	5.2×10^{-2}	1.9×10^{-5}	2.7×10^{0}
pH 7.5	k_B [OH^-] (s^{-1})	3.0×10^{-9}	1.1×10^{-12}	1.6×10^{-7}
[OH^-] = $10^{-7.23}$ M	k_h (s^{-1})	3.0×10^{-9}	2.6×10^{-11}	1.6×10^{-7}
$K_w = 10^{-14.73}$	$t_{1/2}$ (s)	2.3×10^{8}	2.7×10^{10}	4.3×10^{6}
	$t_{1/2}$ (d)	2,700	310,000	50
	I_{NB}	5.0	8.8	4.0

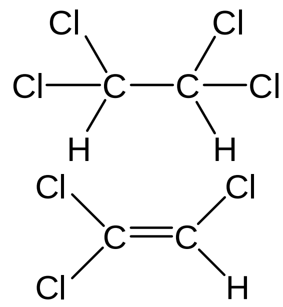




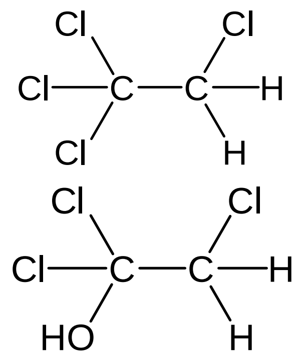


Hydrolysis of Chlorinated Ethanes

- Major products and mechanisms
  - 1,1,2,2-tca ⇒ trichloroethene
    - E_2 elimination, second-order
      - low I_{NB} (4.3): acidic, promotes elimination



  - 1,1,1,2-tca ⇒ 1,1,2-trichloroethanol(?)
    - S_N2 nucleophilic substitution, second order
      - high I_{NB} (8.1): elimination unlikely



  - pentachloroethane ⇒ tetrachloroethene
    - E_2 elimination, second-order
      - even lower I_{NB} (3.5) promotes elimination