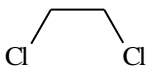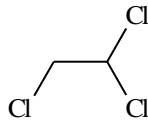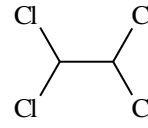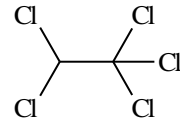# CHEM 331
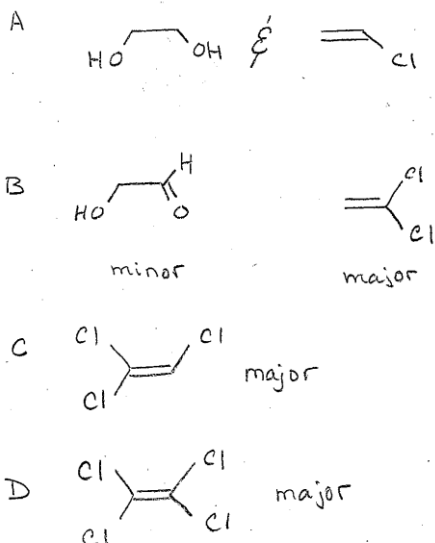## Problem Set #4: Transformations and Kinetics
Hand in worked solutions for even numbered questions for optional grading.
Due: Friday, April 15, 2016

1. Provide the dominant hydrolysis and non-reductive elimination products for each of the following compounds. Explain the observed trend in the k_B values reported below at 25°C for the base enhanced degradation pathway.

	A	B	C	D
k_B (M^{-1}.s^{-1})	1.7×10^{-6}	1.6×10^{-3}	0.50	22
k_N (s^{-1})	3.0×10^{-10}	8.7×10^{-13}	1.6×10^{-10}	8.2×10^{-10}

Solution:

There are a couple of general rules to bear in mind with hydrolysis/elimination reactions of alkyl halides. Firstly, the neutral hydrolysis (as measured by k_N) involving H$_2$O as the nucleophile favours substitution products (i.e., alcohols), whereas the base catalyzed process (k_B) favours elimination products (i.e., alkenes). Secondly, for polyhalogenated aliphatics elimination is favoured over substitution. Finally, it is worth noting that the rate constants refer to loss of starting material and are not specifically associated with either substitution or elimination products. In the question we are asked to explain the trend in k_B values which clearly increase with the extent of chlorination for di-through pentachloroethane. The trend needs to be explained in terms of OH- acting as nucleophile/base. If we take the approach that substitution is occurring the mechanism is likely shifting from S$_N$2 like in the case of A to S$_N$1 like in the case of D. S$_N$1 reactions are faster than S$_N$2 all else being equal given that S$_N$1 only occurs when the transition state leading to formation of the carbocation is lower than that of the pentavalent S$_N$2 transition state. However, given that elimination reactions tend to increase with increasing halogenation, the trend is probably best explained in terms of the increased acidity of the β-hydrogens. The acidity of these hydrogens is governed by the stability of the corresponding conjugate base (carbanion), which is influenced by the number and proximity of the electron withdrawing chlorine atoms present.

2. The hydrolysis half-life for N-methylethanamide at 25°C and pH 7 is 3.78 x 10^4 years. Given that k_B is 5.5 x 10^{-6} $M^{-1}.s^{-1}$ at 25°C and k_N is negligible, calculate k_A in $M^{-1}.s^{-1}$ at 25°C.

Solution: Given that in general, the overall observed rate constant for hydrolysis is;

$k_h = k_A [H^+] + k_N + k_B [OH^-]$

and for amide hydrolysis, $k_N \sim 0$, so we have;

$k_h = k_A [H^+] + k_B [OH^-]$

Since hydrolysis is a *pseudo* first order process (at least when $[H^+]$ and $[OH^-]$ are constant), we can relate the half life to the value of k_h.

$k_h = 0.693/t_{1/2} = 1.83$ x 10^{-5} $yrs^{-1} = 5.81$ x 10^{-13} s^{-1}

Therefore, we can determine k_A using the given pH and k_B values.

$k_A = (k_h - k_B[OH^-])/ [H^+] = \textbf{3.1 x } \mathbf{10^{-7}}\textbf{ M}^{\textbf{-1}}\textbf{ s}^{\textbf{-1}}$

3. The hydrolysis half-life of trimethylphosphate (TMP) in pure water is 438 days at 25°C and pH 7. Your colleague in oceanography, claims that in sterile seawater, she observed a half-life for TMP of only 44 days at 25°C and pH 7. Is this result reasonable? What is the major product of the abiotic transformation of TMP in seawater? Assume that seawater is 0.55 M NaCl. How fast will TMP be transformed by chemical reactions at 10°C and pH 8.0 in a leachate from a waste disposal site containing 0.25 M Cl^-, 0.05 M Br^-, and 10^{-4} M CN^-. Calculate the approximate half-life of TMP under these conditions by trusting your colleague's measurements and by assuming that all relevant reactions exhibit about the same activation energy of 90 kJ.mol^{-1}. Use a value of 1.6 x 10^{-4} $M^{-1}.s^{-1}$ for the k_B of TMP at 25°C and pK_w at 10°C is 14.53

$$CH_3O—\overset{\overset{O}{\|}}{\underset{\underset{OCH_3}{|}}{P}}—OCH_3$$

TMP
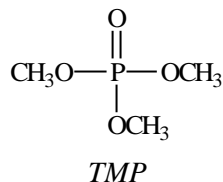
Solution:

       This question has several parts, which we will take in turn. We will first use the half-life data in pure water to determine the value of k_N and in turn, k_{H2O}. Since k_B is given, we can check if k_h has contributions from both H_2O and OH^- at pH 7. We will then use the Swain-Scott approach to determine the rate constants for the other nucleophiles present in ground water (Cl^-, Br^-, CN^-). Strictly speaking, this approach only applies when comparing different nucleophiles reacting with the same electrophile (this may not be the case with TMP, see figure below). We can then write the overall observed pseudo first order rate constant ($k_{obs} = \Sigma\, k_{Nu}$ [Nu]. We will then adjust this rate constant for temperature effects using the Arrhenius equation and estimate the half life in ground water at 10°C using $t_{1/2} = \ln 2/k_{obs}'$. A general reaction scheme that summarizes nucleophilic substitution reactions appears below;
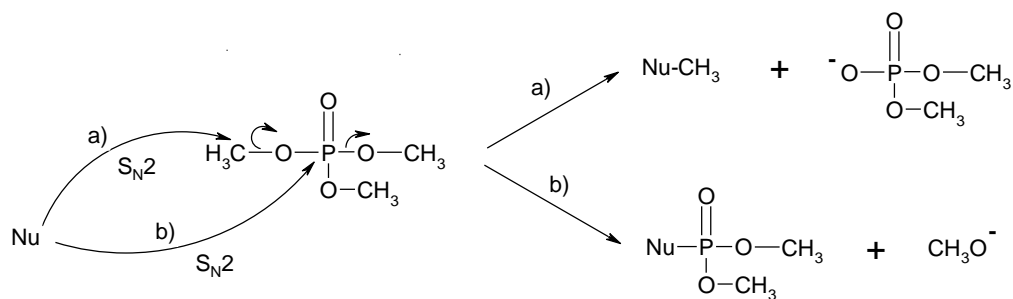
a) = 'soft' nucleophile (e.g., H_2O, Br^-, CN^-)
b) = 'hard' nucleophile (e.g., OH^-, Cl^-)

So here we go….

Pure Water
Since the half-life in pure water is given at 25°C and pH 7, we can calculate the *pseudo* first order rate constant.

$t_{1/2}$ = 438 days, so k_h = 0.693/438 d = **1.58×10^{-3} d^{-1}**.

If we make the assumption that at pH 7 the reaction is dominated by nucleophilic attack by H_2O (i.e., $k_N \gg k_B$ [OH$^-$] at pH 7), then we can write;

$k_h \approx k_N = k_{H2O}$ [H_2O]

Therefore, $k_{H2O} = k_h/[H_2O]$ = 1.58 x 10^{-3} d^{-1}/(55.5 M) = **2.85×10^{-5} d^{-1} M^{-1}**.

Since k_B is given as 1.6 x 10^{-4} M^{-1} s^{-1}, we can compare this to our k_h (above) to check our assumption. At pH 7, the value of k_B [OH$^-$] = 1.6 x 10^{-11} s^{-1}.
Converting this to d^{-1} as follows,

$$k_B \,[OH^-] = 1.6 \times 10^{-11} \, \frac{1}{sec} \times \frac{60 \, sec}{1 \, min} \times \frac{60 \, min}{1 \, hour} \times \frac{24 \, hr}{1 \, d} = 1.38 \times 10^{-6} \, d^{-1}$$

we can see that $k_h \gg k_B$ [OH$^-$] and so $k_h \approx k_N$. Futhermore, we can calculate the isokinetic pH (I_{NB} = 10.1), which also confirms that H_2O is the dominant nucleophile at pH 7.

Seawater
$t_{1/2}$ = 44 days at 25°C, pH 7

So k_{obs}^{sw} = 0.693/44 d = **1.58×10^{-2} d^{-1}**

Since seawater contains nucleophiles other than H_2O, it stands to reason that the half-life of TMP will be shorter in seawater than pure water.

Additional Nucleophiles in Groundwater
Now we want to determine the half-life of TMP in groundwater at 10°C at pH 8 containing 0.25 M Cl$^-$, 0.05 M Br$^-$ and 0.0001 M CN$^-$.

So, $k_{obs}^{gw} = k_{H2O}$ [H_2O] + k_{Cl^-} [Cl$^-$] + k_{Br^-} [Br$^-$] + k_{CN^-} [CN$^-$] + k_B [OH$^-$]

Where we have decided to include the possibility that there is a contribution of OH$^-$ at pH 8. Since all of the nucleophile concentrations are known, all we need to figure out are the specific rate constants for each nuleophile using the Swain-Scott approach and the nucleophilicity '*n*' values in Table 13.3 of the text.

The Swain-Scott equation is given by;

$$\log\left(\frac{k_{Nu}}{k_{H2O}}\right) = ns$$

Thus, we can rearrange for the a specific nucleophile rate constant as;

$$k_{Nu} = k_{H2O} \times 10^{ns}$$

So,

$k_{Cl^-} = k_{H2O}$ x 10^{ns} = 2.85 x 10^{-5} d^{-1} M^{-1} x $10^{(3.0)\,(1.0)}$ = 0.0285 d^{-1} M^{-1},
where we have assumed that the susceptibility of the reaction to nucleophilic strength 's', is equal to unity (i.e., the similar to the susceptibility of methyl bromide, CH_3Br).

Similarly,

$k_{Br^-} = k_{H2O}$ x 10^{ns} = 2.85 x 10^{-5} d^{-1} M^{-1} x $10^{(3.9)\,(1.0)}$ = 0.226 d^{-1} M^{-1},

$k_{CN^{--}} = k_{H2O}$ x 10^{ns} = 2.85 x 10^{-5} d^{-1} M^{-1} x $10^{(5.1)\,(1.0)}$ = 3.59 d^{-1} M^{-1},

Since k_B is given as 1.6 x 10^{-4} M^{-1} s^{-1}, we can convert this to 13.8 d^{-1} and include the contribution of OH^- acting as a nucleophile,

At 10°C, the $[OH^-] = 10^{-(pKw - pH)} = 10^{-6.53}$ = 2.95 x 10^{-7} M

Therefore the overall observed rate constant for loss of TMP is given by;

k_{obs}^{gw} = 2.85 x 10^{-5} d^{-1} M^{-1} (55.5 M) + 0.0285 d^{-1} M^{-1} (0.25 M) +
        0.226 d^{-1} M^{-1}(0.05 M) + 3.59 d^{-1} M^{-1} (0.0001 M) +
        13.8 d^{-1} M^{-1} (2.95 x 10^{-7} M)

k_{obs}^{gw} = **0.0203d^{-1} at 25°C**.

Temperature Change in Groundwater
To convert this pseudo first order rate constant to 10°C, we use the Arrhenius equation,

$$\ln\left(\frac{k_{T2}}{k_{T1}}\right) = \frac{-E_{act}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where T_1 = 298 K, T_2 = 283 K and k_{T1} = 0.0203 d^{-1}.

So, $\ln\left(\dfrac{k_{T2}}{0.0203d^{-1}}\right) = \dfrac{-90,000\,Jmol^{-1}}{8.314\,Jmol^{-1}K^{-1}}\left(\dfrac{1}{283K} - \dfrac{1}{298K}\right)$

and k_{T2} = 0.0203 d^{-1} $e^{-1.93}$ = 2.95 x 10^{-3} d^{-1}

THEREFORE THE HALF-LIFE IN GROUNDWATER AT 10°C IS GIVEN BY;

$t_{1/2}$ = 0.693/(2.95 x 10^{-3} d^{-1}) = 240 days!

ASIDE (to check the assumption about the susceptibility term, '*s*'):

Since we are told to assume the seawater is 0.55 M NaCl (i.e., ignore the other nucleophiles, which is reasonable since Cl$^-$ is by far the most abundant anion),

$k_{obs}^{sw} = k_{H2O} [H_2O] + k_{Cl^-} [Cl^-]$ = 1.58 x 10^{-2} d^{-1}

So, $k_{Cl^-} = (k_{obs}^{sw} - k_{H2O} [H_2O])/[Cl^-]$ = 2.59 x 10^{-2} d^{-1} M^{-1}

We can use this value to evaluate the sensitivity of TMP to nucleophilicity ('*s*') using the Swain-Scott approach;

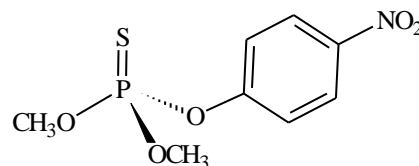$$\log\left(\frac{k_{Cl^-}}{k_{H2O}}\right) = ns$$, where *n* for Cl$^-$ is given as 3.0 in Table 13.3, p. 498 text.

Since k_{Cl^-} and k_{H2O} are known we can calculate,

$$s = \frac{\log\left(\dfrac{k_{Cl^-}}{k_{H2O}}\right)}{n} = \frac{2.96}{3.00} = 0.987 \cong 1.0$$

4. A spill of methylparathion into Long Lake occurs during the month of June (pH 8.5 and 10°C), calculate the half-life from abiotic hydrolysis in years. Speculate on the mechanism of hydrolysis at this pH and temperature. The following data is found in the literature.

k_{hyd} (s^{-1}) for methylparathion			
Temperature (°C)	pH 4	pH 5	pH 11
25	1.20×10^{-7}	1.20×10^{-7}	1.11×10^{-5}
20	5.63×10^{-8}		
10			9.16×10^{-7}

Solution:

There several components to this question including the effect of both pH and temperature on the hydrolysis of methylparathion. The effect of pH can be addressed by breaking down the observed hydrolysis rate constant into a neutral and base enhanced contribution (k_N and k_B).

$$k_h = k_A \, [H^+] \; + \; k_N \; + \; k_B \, [OH^-]$$

The effect of temperature can be addressed by applying the Arrhenius equation and calculating the activation energy (Ea).

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

k_B at 25°C:
The data indicate that there is no acid or base catalysis between pH 4 and 5 at 25°C, so $k_N = 1.20 \times 10^{-7}$ s^{-1}.

We can use this fact and the hydrolysis rate at pH 11 to determine the value of k_B at 25°C.

$$k_B = \frac{\left(k_h - k_N\right)}{[OH^-]} = \frac{\left(1.11 \times 10^{-5} \text{ s}^{-1} - 1.20 \times 10^{-7} \text{ s}^{-1}\right)}{1.00 \times 10^{-3} \text{ M}} = 0.01098 \text{ s}^{-1}\text{ M}^{-1}$$

k_N at 10°C:
First use the values of k_N at 25 and 20 °C to calculate the activation energy for the neutral hydrolysis.

$$\ln\left(\frac{1.20}{0.563}\right) = \frac{-E_a}{8.314 \text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{298} - \frac{1}{293}\right)$$

$$\therefore Ea = \frac{-0.7568 \, (8.314 \text{ J mol}^{-1}\text{ K}^{-1})}{(-5.7 \times 10^{-5} \text{ K}^{-1})} = 110.4 \text{ kJ mol}^{-1}$$

Then use this value of Ea to calculate the value of k_N at 10 °C (283 K).

$$\ln\left(\frac{1.20\times10^{-7}\ s^{-1}}{k_N^{283}}\right) = \frac{-110{,}400\ J\ mol^{-1}}{8.314\ J\ mol^{-1}\ K^{-1}}\left(\frac{1}{298} - \frac{1}{283}\right) = 2.362$$

$$\therefore \frac{1.20\times10^{-7}\ s^{-1}}{k_N^{283}} = e^{2.362} = 10.61$$

So, k_N at 10°C = $(1.20 \times 10^{-7}\ s^{-1})/10.61 = 1.13 \times 10^{-8}\ s^{-1}$

k_B at 10°C:

$$k_h = k_N + k_B\,[OH^-]$$

Using the values of the rate constants at 10 °C; $k_h = 9.16 \times 10^{-7}\ s^{-1}$ (from question) and $k_N = 1.13 \times 10^{-8}\ s^{-1}$ (from above) and $[OH^-] = K_w/[H^+] = 2.95 \times 10^{-4}$ M (using $pK_w = 14.53$ at 10 °C), we can calculate;

$$k_B = \frac{(k_h - k_N)}{[OH^-]} = \frac{(9.16\times10^{-7}\ s^{-1} - 1.13\times10^{-8}\ s^{-1})}{2.95\times10^{-4}\ M} = 3.07\times10^{-3}\ s^{-1}\ M^{-1}$$

k_h at pH 8.5 and 10 °C:

$$k_h = k_N + k_B\,[OH^-] = 1.13\times10^{-8}\ s^{-1} + 3.07\times10^{-3}\ s^{-1}\ M^{-1}\ (10^{-14.53}/10^{-8.50}) = 1.42\times10^{-8}\ s^{-1}$$

So the half-life at this pH and temperature for abiotic hydrolysis is given be;

$$\mathbf{t_{1/2} = 0.693/k_h = 4.89 \times 10^7\ s = 155\ years}$$

Mechanism and hydrolysis products:

Hydrolysis of phosphate esters generally occurs via S_N2 substitution at the alkyl carbon under conditions where H_2O is acting as the nucleophile and at the phosphorous centre when OH^- as the dominant nucleophile. In order to establish the dominant pathway under the specified conditions, we need to calculate the *isokinetic* pH (I_{NB}).

At the isokinetic pH, we can write $k_N = k_B\,[OH^-]$.

Rearranging yields, $[OH^-] = k_N/k_B = 3.68 \times 10^{-6}$ M
Since $pH + pOH = pKw = 14.53$ (at 10 °C), we have $pH = 14.53 - 5.43 = 9.10$

Since the pH of Long Lake is $< I_{NB}$, the dominant hydrolysis is occurring via H_2O attack on the alkyl group leading to the following as the dominant products;
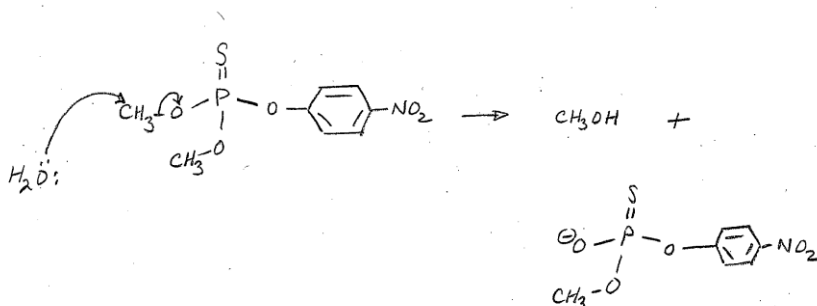
5. The oxidation kinetics of a series of substituted phenols by $HCrO_4^-$ at conditions present in contaminated sites. At a fixed pH = 2, the reaction can be described by an empirical *pseudo*-second order rate law;

$$-d(ArOH)/dt = k_{ArOH} \bullet [ArOH][HCrO_4^-]$$

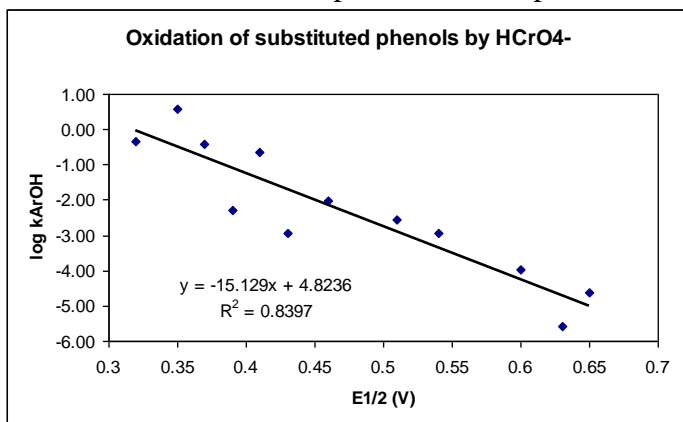A plot of log k_{ArOH} versus $E_{1/2}$ yields a LFER with some degree of scatter; slope = -15.1, $r^2 = 0.83$.
a) Are there a subset of compounds that yield a much better LFER?
b) Estimate the k_{ArOH} values of trace 3,5-dimethoxyphenol ($E_{1/2} = 0.60$ V) using the refined LFER above and calculate its half-life in a solution containing 1.0 mM chromate at pH 2.
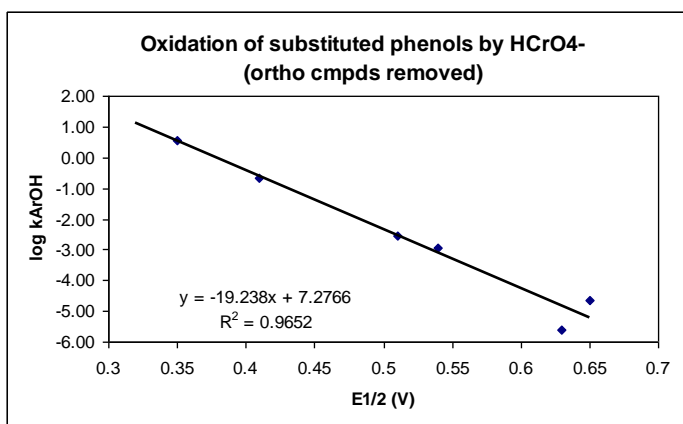
Compound	k_{ArOH} (M^{-1} s^{-1})	$E_{1/2}$ (V) vs SCE
phenol	2.6 x 10^{-6}	0.63
4-methylphenol	1.2 x 10^{-3}	0.54
2,4-dimethylphenol	9.4 x 10^{-3}	0.46
3,4-dimethylphenol	2.8 x 10^{-3}	0.51
2,6-dimethylphenol	1.2 x 10^{-3}	0.43
2,4,6-trimethylphenol	5.3 x 10^{-3}	0.39
4-methoxyphenol	2.2 x 10^{-1}	0.41
2,6-dimethoxyphenol	4.4 x 10^{-1}	0.32
3,4-dimethoxyphenol	3.7 x 10^{0}	0.35
2-methoxy-4-CHO-phenol	1.1 x 10^{-4}	0.60
2-methoxy-4-methylphenol	3.8 x 10^{-1}	0.37
4-chlorophenol	2.3 x 10^{-5}	0.65

Elovitz et al, *Environ. Sci. Technol.*, **1994**, *28*, 2161-2169; **1995**, *29*, 1993-1943.

Solution:

a) Using all of the kinetic data given in the question, a plot of log k_{ArOH} versus $E_{1/2}$ yields a line with slope = -15.1, with an $R^2 = 0.83$. The degree of scatter can be improved by removing the *ortho* substituted phenols which are influenced by steric factors in addition to electronic ones. Without the 2-substituted phenols, the slope = -19.2 and the R^2 improves to 0.97.
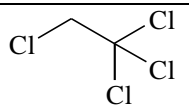

Oxidation of substituted phenols by HCrO4-

$y = -15.129x + 4.8236$
$R^2 = 0.8397$

**Oxidation of substituted phenols by HCrO4-
(ortho cmpds removed)**

$y = -19.238x + 7.2766$
$R^2 = 0.9652$

x-axis: **E1/2 (V)**
y-axis: **log kArOH**

b) Using the refined LFER ($\log k_{\text{ArOH}} = -19.1 * E_{1/2} + 7.27$), we can estimate the k_{ArOH} for 3,5-dimethoxyphenol ($E_{1/2} = 0.60$V) at 6.5×10^{-5} M^{-1} s^{-1}. Therefore, the *pseudo* first order rate constant when [HCrO4-] = 1×10^{-3} M, is given by k_{ArOH} ([HCrO4-]) = k_{obs} = 6.5×10^{-8} s^{-1} and so the half-life is equal to $0.693/6.5 \times 10^{-8}$ s^{-1} = 1.1×10^{7} s = **120 days**.

6. Given the kinetic information below for the hydrolysis/elimination of 1,1,2,2-tetrachloroethane at 25ºC, calculate the number of years required for 90% degradation via abiotic hydrolysis/elimination in the hypolimnion of a lake (T = 5ºC, pH 8.8). (Note; pK_w at 5ºC = 14.73).

	k_N (s^{-1})	E_a (kJ mol^{-1})	k_B (M^{-1} s^{-1})	E_a (kJ mol^{-1})
CHCl$_2$-CHCl$_2$	1.6 x 10^{-11}	93	2.0 x 10^{-6}	78

b) Use the following information for 1,1,1,2-tetrachloroethane at 25°C to answer the following.

Pollutant	k_N (s^{-1})	k_B (M^{-1}.s^{-1})
Cl$\diagup$$\diagdown$Cl $\diagdown$Cl $\diagdown$Cl (Cl)	2.60 x 10^{-8}	2.15 x 10^{-2}

   i) Provide the mechanism of the reaction that dominants at pH 8.5 and 25 ºC.
   ii) What is the half-life of 1,1,1,2-tetrachloroethane at pH 7.0 and 25 ºC (conditions).

Solution:

   a) There are three parts to the solution here. The first is to adjust the given rate constants from 298 K to 278 K using the Arrhenius equation. The second part will involve making use of the pH to calculate the [OH$^-$] and hence k_h at pH = 8.8. Finally, we will determine the time required for 90% degradation using the integrated first order rate equation and the fact that [TCE] at 90% degradation = 0.10 of the initial [TCE].

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

So, use the values of k_N at 298 and Ea = 93,000 J mol-1, we get

Then use this value of Ea to calculate the value of k_N at 10 ºC (283 K).

$$\ln\left(\frac{1.60\text{x}10^{-11}\text{ s}^{-1}}{k_N{}^{278}}\right) = \frac{-93,000 \text{ J mol}^{-1}}{8.314 \text{J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{298} - \frac{1}{278}\right) = 2.700$$

$$\therefore \frac{1.60 \times 10^{-11}\text{ s}^{-1}}{k_N{}^{283}} = e^{2.700} = 14.89$$

So, k_N at 5ºC = (1.60 x 10^{-11} s^{-1})/14.89 = **1.07 x 10^{-12} s^{-1}**

Similarly for k_B, we get

k_B at 5ºC = (2.0 x 10^{-6} M^{-1} s^{-1})/9.629 = **2.08 x 10^{-7} M^{-1} s^{-1}**

$$pOH = pK_w - pH = 14.73 - 8.8 = 5.93$$

Therefore, $[OH^-] = 10^{-5.93} = 1.17 \times 10^{-6}$ M

And, $k_h = k_N + k_B[OH^-] = (1.07 \times 10^{-12} \text{ s}^{-1} + (2.08 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1} \times 1.17 \times 10^{-6} \text{ M}) = \mathbf{1.31 \times 10^{-12} \text{ s}^{-1}}$
Substituting this into the first order integrate rate equation and solving for time yields;

$$\ln\left(\frac{[A]t}{[A]o}\right) = -kt$$

Where $[A]_t/[A]_o = 0.10$ and ln $(0.10) = 1.105$

So $t = (1.105)/1.31 \times 10^{-12} \text{ s}^{-1}) = 8.44 \times 10^{11}$ s $= \mathbf{2.68 \times 10^4}$ **years**.

b)
i) Since rate constants are given at 25 ºC, there is no need to adjust for temperature here. We can compare k_N to $k_B[OH^-]$ at pH 8.5 to determine whether neutral hydrolysis or base catalyzed elimination dominates. At pH = 8.5 and 25 ºC, we can write pOH = 14.0 – 8.5. Therefore, $[OH^-] = 3.16 \times 10^{-6}$ M and $k_B[OH^-] = 6.8 \times 10^{-8}$ which is greater than k_N. So, the elimination reaction yielding trichloroethene will dominate. The likely mechanism will be E2 (concerted bimolecular).

ii) The half-life is determined from the pseudo first order rate constant (k_h), which is equal to k_N + $k_B[OH^-]$. At 25 ºC, $k_h = 2.60 \times 10^{-8} + 2.15 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ (1.00 $\times 10^{-7}$ M) $= 2.81_5 \times 10^{-8} \text{ s}^{-1}$.
So $t_{1/2} = 0.693/2.82 \times 10^{-8} \text{ s}^{-1} = 2.46 \times 10^7$ s $= \mathbf{285 \text{ days}}$.

7. Under anaerobic conditions the following halogenated ethanes undergo a reaction known as *vicinal dehalogenation*.

a) Suggest an explanation for the observed trend in the *pseudo* first order rate constants (k_{obs}) increasing with increased halogenation.

b) What are the products in each case and why are they environmentally relevant?

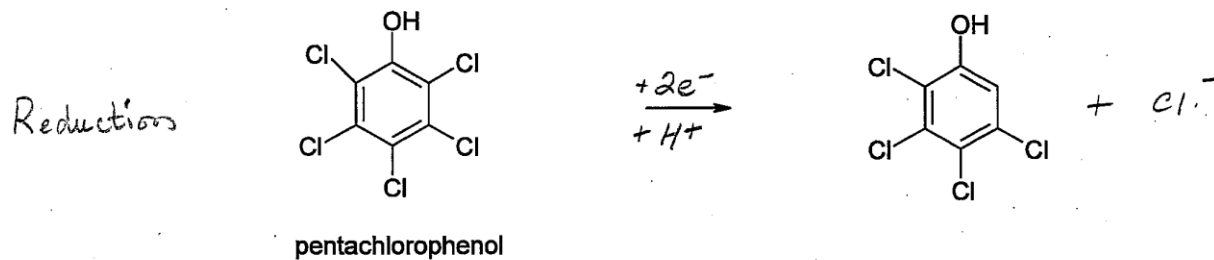| Structure	k_{obs} (s^{-1})
CH_2Cl-CH_2Cl	$< 2 \times 10^{-7}$
$CHCl_2$-$CHCl_2$	1.2×10^{-6}
CCl_3-CCl_3	3.2×10^{-4}

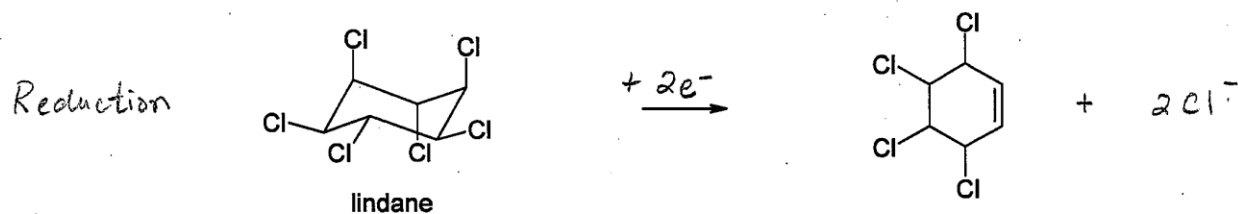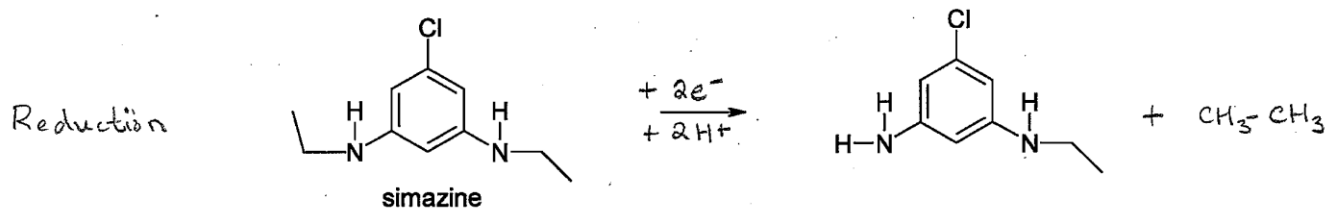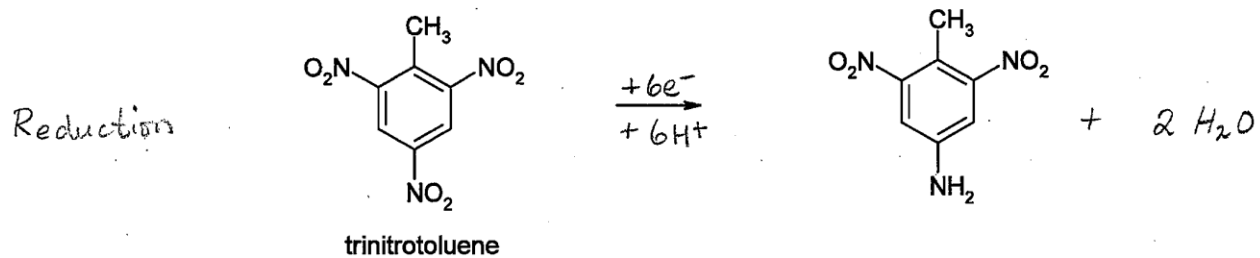*Solution:*

a) The compounds listed are a series of symmetrical polychlorinated ethanes (CCl_nH_{3-n}-CCl_nH_{3-n}), where n = 1,2,3. In general, the reduction rates of alkyl halides is inversely correlated with C-X bond strength. The more chlorinated ethanes have weaker C-Cl bonds due to steric crowding. Remember any discussion of kinetic trends is really about the relative energy of the transition state (activated complex) involved in the rate determining step. These reductions are the result of the addition of an electron to the carbon-halogen bond. The one-electron reduction potentials for organic compounds in aqueous solution are not generally available, so we will take a more qualitative approach by considering the factors that influence the free-energy of the transition state.

Although the details of the mechanism are not fully understood, the first step involves accepting an electron, which results in the C-X bond becoming partially dissociated (since the electron must occupy an anti-bonding orbital). It subsequently cleaves to yield a halide ion and a carbon centred radical. Hence, the factors that may influence the energetics include the electron accepting ability of the substrate (which is related to the electronegativity of the halogens involved), the C-X bond strength and stability of the resulting carbon centred radical. Hexachloroethane undergoes vicinal dehalogenation about 1000X faster than 1,2-dichloroethane due to its greater electron accepting ability (more electronegative Cl atoms) and weaker C-Cl bond strength (steric crowding).

b) The products are ethene, 1,2-dichloroethene and 1,1,2,2-tetrachloroethene, respectively. Halogenated alkenes are environmentally relevant due to their persistence (resistance to hydrolysis) and tendency to bio-accumulate (relatively high Kow values).

8. a) Identify each of the following reactions as either oxidation or reduction and write the balanced half reaction.

Reduction

trinitrotoluene

$+ 6e^-$
$+ 6H^+$

$+ \quad 2 H_2O$

Reduction

simazine

$+ 2e^-$
$+ 2H^+$

$+ \quad CH_3-CH_3$

Reduction

lindane

$+ 2e^-$

$+ \quad 2Cl^-$

Reduction

pentachlorophenol

$+ 2e^-$
$+ H^+$

$+ \quad Cl^-$

Oxidation

17-α estradiol

$+ 2 \, HOCl$

$+ \quad 2 H_2O$
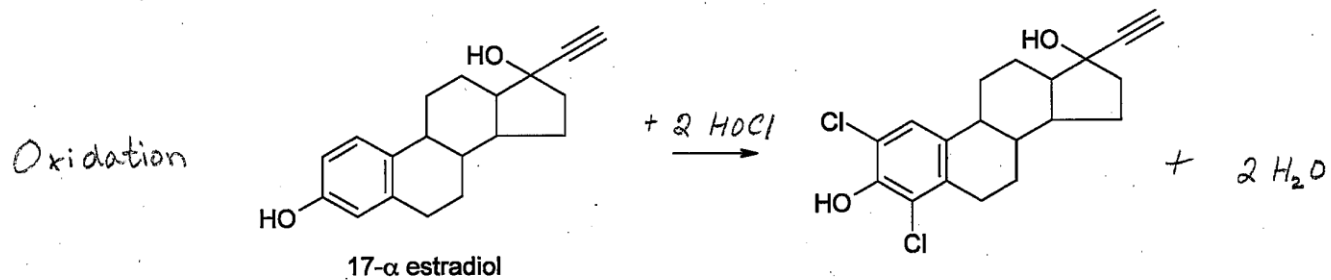
b) Predict the major hydrolysis product/s and suggest a mechanism in each case.

H₂Ö:
H⁺ (cat.)

H₂O
OH-

H₂O
H⁺ (cat.)

H₂O

OH-

dimerization

2,3,7,8-TCDD