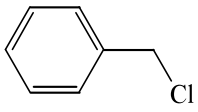
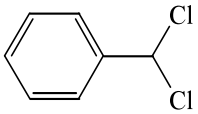
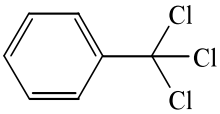
CHEM 331
Problem Set #4: Transformations and Kinetics

1. a) The hydrolysis half-lives of three benzylic chlorides at pH 7 and 25°C are given below. In each case predict the stable hydrolysis product/s. Propose a mechanism and explain why the rate of the reaction increases with halogenation.

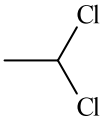


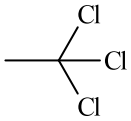




Half-life	15 hrs	6 min	19 s

b) Explain the neutral rate constant for loss of 1,1-dichloroethane is considerably faster than that of 1,1,1-trichloroethane in aqueous solution. Be sure to include the dominant mechanism in your answer

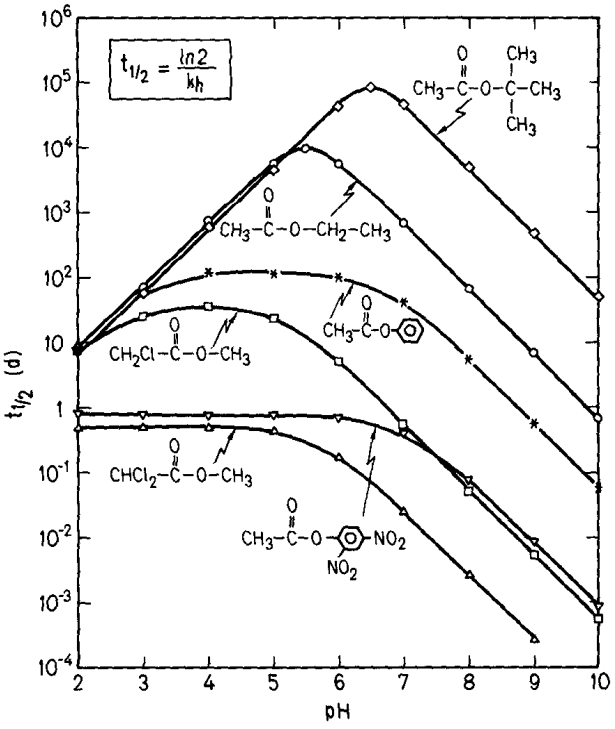




k_N (s^{-1}) at 25°C	3.0×10^{-10}	8.7×10^{-13}

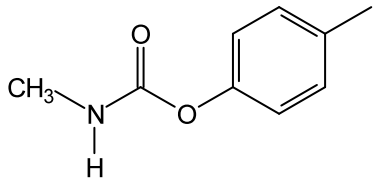
2. Estimate the half-life for the hydrolysis of chloromethane in a waste pond at pH 10.6 and 25°C that contains 1.10 mM CN^- and 4.65 M NO_3^-. The half-life of CH_3Cl in pure water at 25°C and pH 7 is 329 days. Provide the major product.

3. Use the following figure to estimate each of the following;
a) k_B for 2,4-dinitrophenyl acetate
b) an upper limit for the k_N of t-butyl acetate



4. If ten kilograms (10.0 kg) of 4-methylphenyl N-methyl carbamate is spilled into a lake during the month of April (pH 7.5 and 5°C), calculate the amount (in kg) eliminated 90 days later by abiotic hydrolysis. Speculate on the mechanism. Assume at pH 12 the dominant mechanism is base catalysis. Acid catalysis of carbamates can be neglected while the neutral reaction may be significant. The following data was found in the literature.

k_{hyd} (s^{-1})			
Temperature (°C)	pH 7	pH 8	pH 12
25	1.16×10^{-7}		5.60×10^{-3}
20		3.14×10^{-7}	2.82×10^{-3}
5			2.85×10^{-4}



5. a) What is an electron transfer mediator? Give an example of an environmentally relevant species that may act as a mediator.
b) Identify four naturally occurring oxidizing agents and briefly indicate how they are formed in the environment.

6. It has been demonstrated that natural organic matter (NOM) from a variety of sources mediates the reduction of nitroaromatic compounds (NACs) in aqueous solution containing hydrogen sulphide (H_2S) as a bulk electron donor. They found that in the absence of NOM, the reduction of the NACs investigated occurred extremely slowly. For a given NOM and system conditions (pH, T, and $[H_2S]_{tot}$) they defined a carbon-normalized second-order rate constant (k_{NOM}), which describes the reduction rate of a series of substituted nitrobenzenes ($ArNO_2$) by the second-order rate law, where [NOM] is the total organic carbon concentration expressed in mg C/L;

$$-d(ArNO_2)/dt = k_{NOM} \bullet [ArNO_2][NOM]$$

The second order rate constants for 10 monosubstituted nitrobenzenes are summarized along with the one-electron reduction potentials below.

Compound (X-$ArNO_2$)	X	$E_H^{1'}(ArNO_2)$[a] Volts	k_{NOM} (hr^{-1} (mg C/L)$^{-1}$)
nitrobenzene	H	-0.485	4.5×10^{-5}
2-methylnitrobenzene	2-Me	-0.590	3.0×10^{-6}
3-methylnitrobenzene	3-Me	-0.475	6.6×10^{-5}
4-methylnitrobenzene	4-Me	-0.500	2.9×10^{-5}
2-chloronitrobenzene	2-Cl	-0.485	1.6×10^{-4}
3-chloronitrobenzene	3-Cl	-0.405	8.1×10^{-4}
4-chloronitrobenzene	4-Cl	-0.450	3.6×10^{-4}
2-acetylnitrobenzene	2-$COCH_3$	-0.475	3.8×10^{-4}
3-acetylnitrobenzene	3-$COCH_3$	-0.405	1.0×10^{-3}
4-acetylnitrobenzene	4-$COCH_3$	-0.360	3.3×10^{-2}

[a] $E_H^{1'}(ArNO_2)$ is the reduction potential of the half-reaction below;

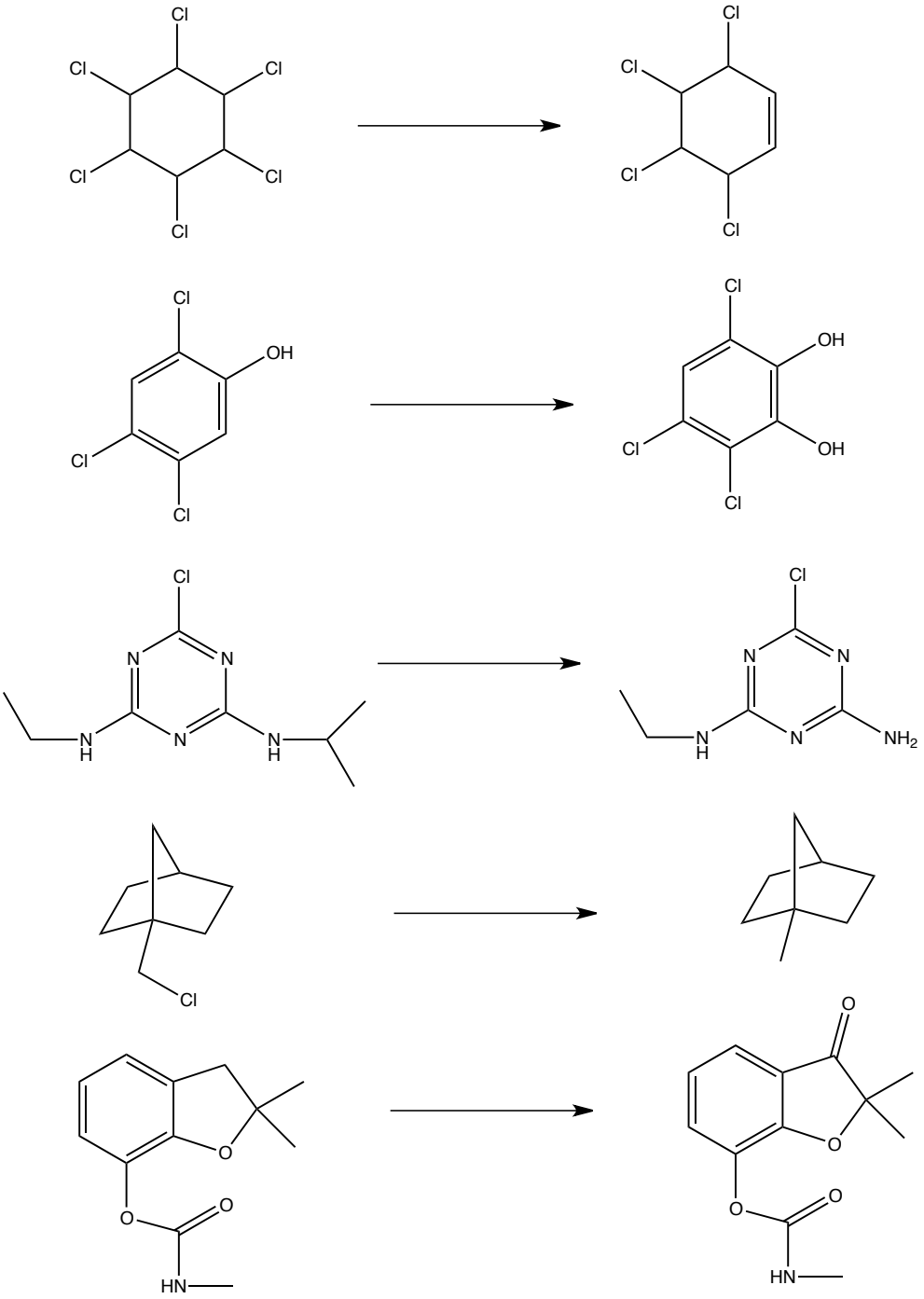
$$ArNO_2 + e^- \rightarrow ArNO_2^{\bullet -} \text{ (pH 7, 25°C)}$$

Dunnivant et al., *Environ. Sci. Technol.*, *26*, 2133 – 2141 (**1992**)

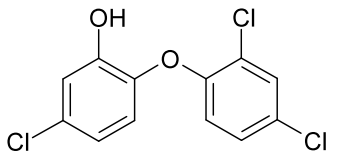
a) Is the electron transfer between reduced NOM molecules and the NACs rate-determining?
b) Estimate the $E_H^{1'}(ArNO_2)$ value of 1,3-dinitrobenzene, using Hammett substituent constants.
c) Estimate the half-life of 1,3-dinitrobenzene in an aqueous solution (25°C, 5mM H_2S, pH 7) containing 5 mg C/L NOM.

7. Provide two classes of organic dis-infection by-products resulting from the oxidation of natural organic matter by active chlorine that are regulated in the United States. Identify two additional classes of dis-infection by-products that have emerged in the past decade and indicate specific precursors, if any. See further Krasner et al., *Environ. Sci. Technol.*, *40*, 7175-7185 (**2006**).

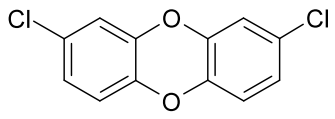
8. a) Identify each of the following reactions as either oxidation or reduction and write the balanced half reaction.

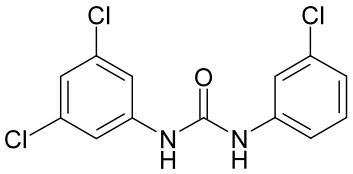


b) Propose a mechanism for each of the following transformations.

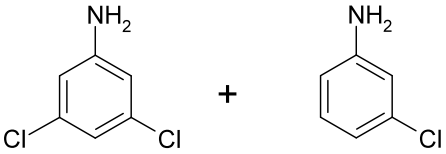


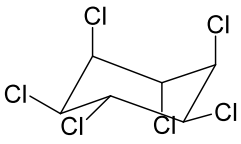
triclosan



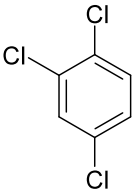


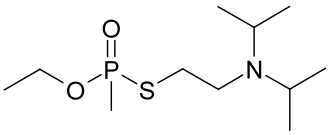
triclocarban



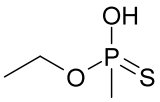


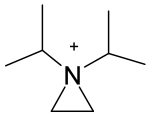
lindane

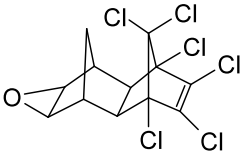




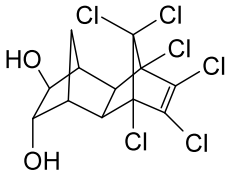
VX

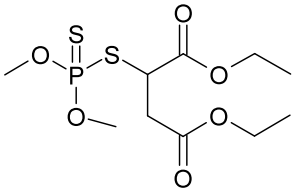




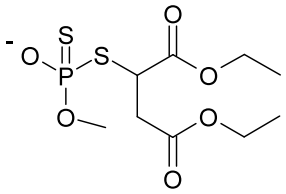


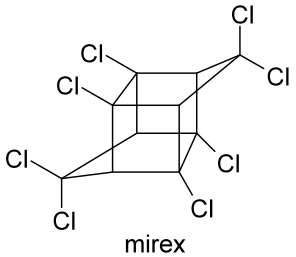
endrin





malathion





mirex