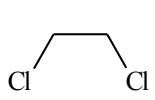
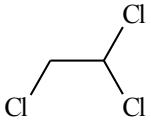
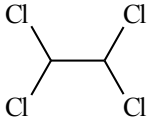
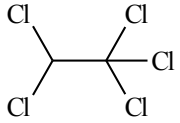
CHEM 331

Problem Set #4: Transformations and Kinetics

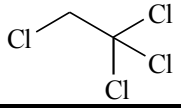
Hand in all worked solutions in a neat and organized format. Not all questions will be graded.

Due: Friday, Apr 13th.

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}

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

Pollutant	k_N (s^{-1})	k_B ($M^{-1}.s^{-1}$)
	2.60×10^{-8}	2.15×10^{-2}

a) Provide the mechanism of the reaction that dominants at pH 8.5 and 25 °C.

b) What is the half-life of 1,1,1,2-tetrachloroethane at pH 7.0 and 25 °C.

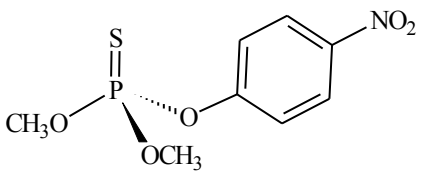
3. Given the kinetic information below for the hydrolysis/elimination of 1,1,2,2-tetrachloroethane at 25°C, calculate the number of years required for 90% degradation via abiotic hydrolysis/elimination in the hypolimnion of a lake (T = 5°C, pH 8.8). (Note; pK_w at 5°C = 14.73).

	k_N (s^{-1})	E_a (kJ mol^{-1})	k_B (M^{-1} s^{-1})	E_a (kJ mol^{-1})
$CHCl_2$-$CHCl_2$	1.6×10^{-11}	93	2.0×10^{-6}	78

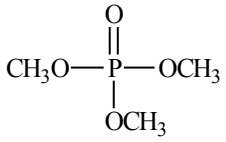
4. The hydrolysis half-life for N-methylethanamide at 25°C and pH 7 is 3.78×10^4 years. Given that k_B is 5.5×10^{-6} M^{-1} s^{-1} at 25°C and k_N is negligible, calculate k_A in M^{-1} s^{-1} at 25°C. Write a stepwise mechanism the acid catalyzed hydrolysis of this amide.

5. 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}



6. 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



TMP

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 x 10^{-7}
$CHCl_2$-$CHCl_2$	1.2 x 10^{-6}
CCl_3-CCl_3	3.2 x 10^{-4}

8. The rate constant for the chlorination of a series of substituted phenols correlate with the pK_a of the corresponding phenol. What does this suggest about the rate-determining step? What are the identified disinfection by-products of phenol?

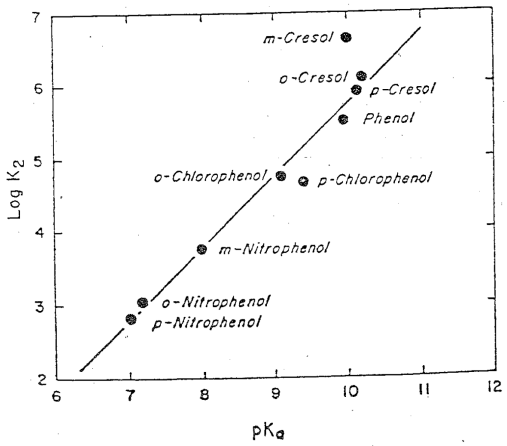
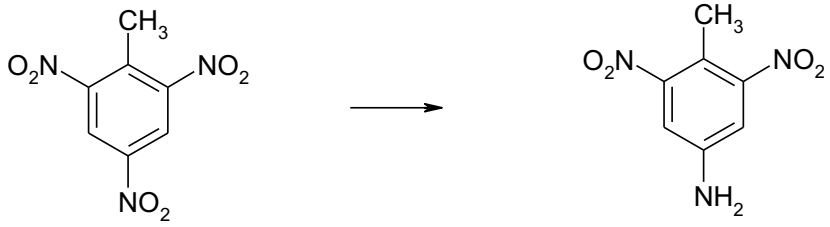


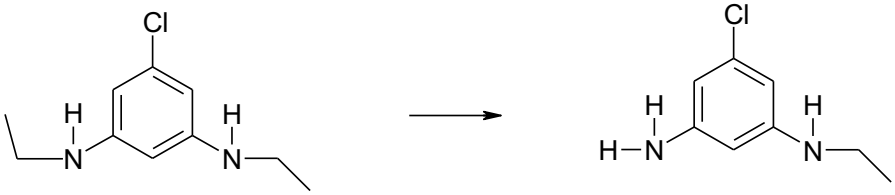
Figure 5.2. Effect of phenol acidities on the rate constants of their reactions with HOCl. From Soper and Smith (1926). Reprinted by permission of the Royal Society of Chemistry (U.K.).

From Reaction Mechanisms in Environmental Organic Chemistry, R.J. Larson & E.J. Weber, CRC Press, 1994, p.280.

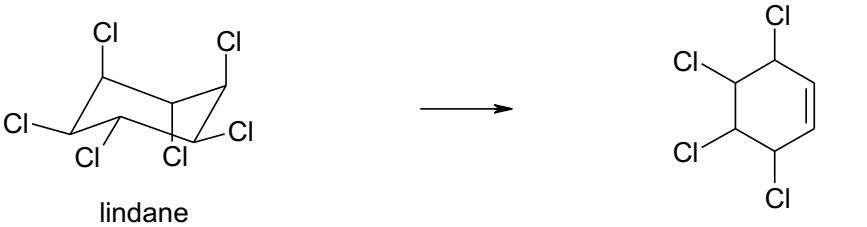
9. Identify each of the following reactions as either oxidation or reduction and write the balanced half reaction.



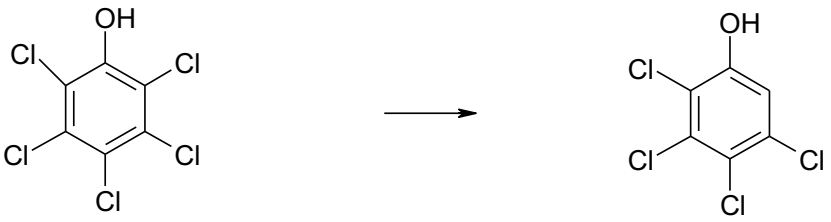
trinitrotoluene



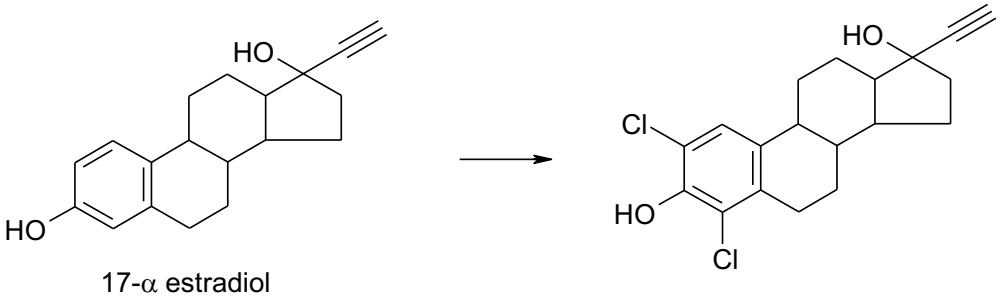
simazine



lindane

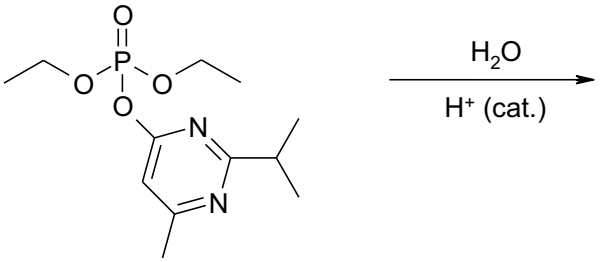


pentachlorophenol



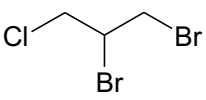
17-α estradiol

10. Predict the major hydrolysis product/s and suggest a mechanism in each case.



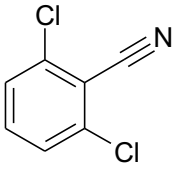
H_2O

H^+ (cat.)



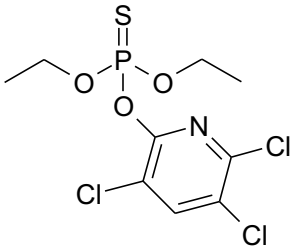
H_2O

OH-



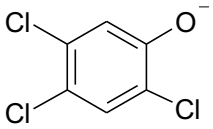
H_2O

H^+ (cat.)



H_2O

OH-



dimerization

2,3,7,8-TCDD