Review Questions for CHEM 331 Final

Topic Breakdown

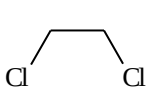
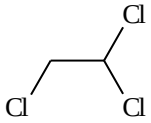
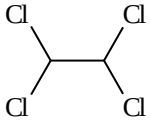
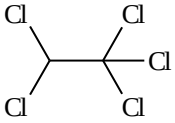
- ~30% Intrinsic & Physical Properties, Partitioning and Distribution
- ~30% Substituent Effects & Hydrolysis / Elimination
- ~20% Redox Reactions
- ~20% Integrated

Possible discussion topics

- Fate and distribution of organic contaminants
- Solubility and activity of organic compounds in water
- LFERs (phys properties, K_{eq} and kinetics)
- Property estimation methods
- Structure – Activity relationships
- Substituent Effects, Hammett and Hammond
- Environmental conditions and chemical transformations
- Redox behaviours and role of electron transfer mediators

Sample Questions

1. Answer the following questions using the rate constant data at 25°C below:

	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}

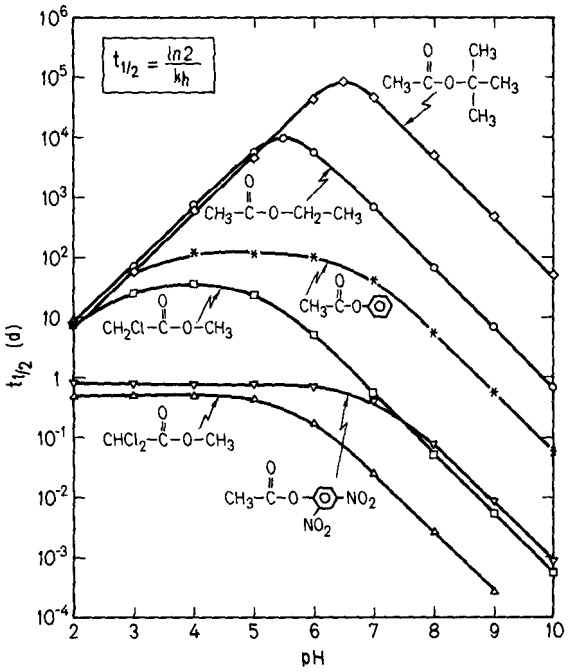
a) In each case, indicate the product/s of hydrolysis, elimination and reduction.

b) What would you expect the major product for the reaction of 1,2-dichloroethane, A in aerated waters at pH 7 and 25°C? Justify your answer.

2. Interpret the following σ values in terms of the electronic character of each group. Discuss the inductive and resonance effects, using examples showing resonance structures when appropriate, using phenol as an example.

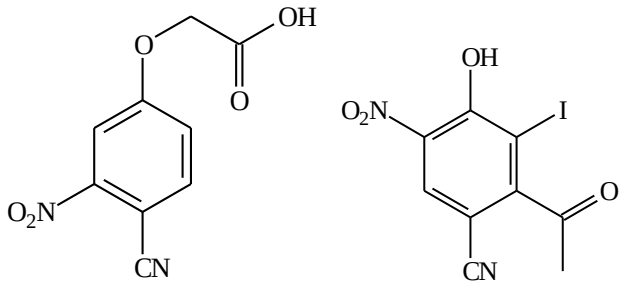
Substituent	σ_{meta}	σ_{para}	σ^-_{para}
$-NO_2$	0.71		1.25
$-N(CH_3)_3^+$	0.88	0.82	

3. Use the half-life at pH 2 on the following pH profile for various carboxylic acid esters to calculate/estimate k_A for:

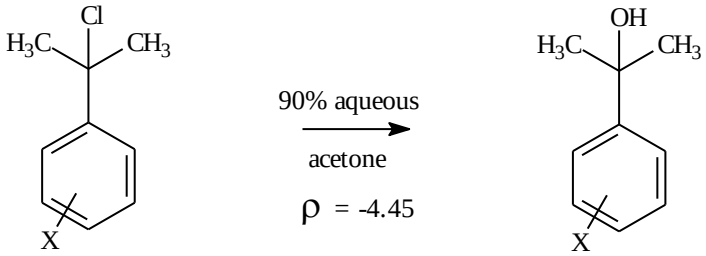


a) methyl 2,2-dichloroethanoate, $Cl_2CHCOOCH_3$
b) ethyl acetate, CH_3COOEt

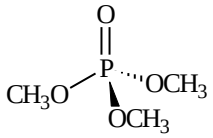
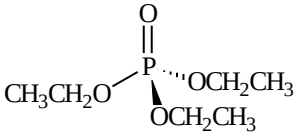
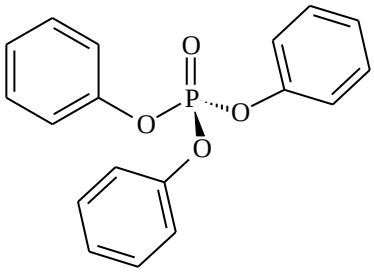
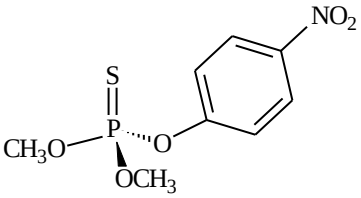
4. Estimate the pK_a values at 25°C of the following:



5. For the following reaction:
   a) Provide the stepwise mechanism.
   b) Sketch the Energy versus the Reaction Coordinate diagram.
   c) Sketch the transition state showing charge development.
   d) Explain the value of the susceptibility constant.
   e) Indicate which σ scale was used and why.



6. Consider the data and answer the following questions. [5marks]

Name	Structure	k_A ($M^{-1}.s^{-1}$)	k_N (s^{-1})	k_B ($M^{-1}.s^{-1}$)
Trimethylphosphate		NI	1.8×10^{-8}	1.6×10^{-4}
Triethylphosphate		NI	4×10^{-9}	8.2×10^{-6}
Triphenylphosphate		NI	3×10^{-9}	0.25
Methylparathion		NI	1.2×10^{-7}	1.1×10^{-2}

NI = not important

a) Studies have shown that the attack of a nucleophile on phosphorus proceeds via an S_N2 mechanism. The Swain Scott value *n* for hydroxide is 4.2. Taking this into account and considering k_N and k_B for triphenylphosphate, how much more effective is hydroxide as a nucleophile in attacking phosphorus over carbon? You must give a clear and logical argument.

b) Provide the major product/s for the k_B mechanism of methylparathion

c) Provide the major product/s for the k_N mechanism for triphenylphosphate

d) Provide an explanation why k_B for trimethylphosphate is greater than k_B for triethylphosphate.

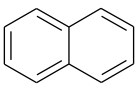
7. Write the balanced half-reaction for the transformation of 1,1,1,2,2,2-hexachloroethane to 1,1,2,2-tetrachloroethene under. Suggest a bulk reducing agent and redox mediator in the environment and explain the role of each.

8. The following data on 1,2,4,5-tetramethylbenzene or durene (TMB) is available in the CRC Handbook of Chemistry and Physics: normal melting point (T_m) 79.5°C, normal boiling point (T_b) 195.9°C

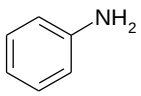
Temperature, T (°C)	Vapor Pressure, P^o (mm Hg)
45.0 s	1
74.6 s	10
104.2	40
128.1	100
172.1	400
195.9	760

a) Calculate the vapour pressure, P^o in atmospheres of TMB at 20°C and report the result in mg m^{-3}. Note that at 20°C TMB is a solid and you need to find the vapor pressure of the solid. Since $\Delta H_{sub} = \Delta H_{fusion} + \Delta H_{vap}$ this line will have a different slope than that of the liquid ($-\Delta H_{vap} / R$).
b) Calculate the vapor pressure of the subcooled liquid of TMB at 20°C using the data given above.

9. Calculate the activity coefficients for naphthalene and aniline in water and water-saturated 1-octanol at 25°C using the data given below. Comment on your results and indicate whether the value of K_{ow} is more influenced by solubility of organics in water or 1-octanol.



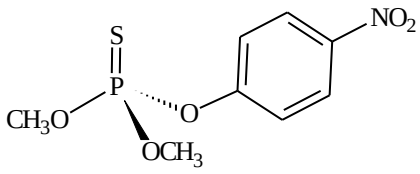
MW = 128.2 g mol^{-1}
T_m = 80.6 °C
C_w^{sat}(25°C) = 2.5 x 10^{-4} mol L^{-1}
K_{ow} = 2.3 x 10^3



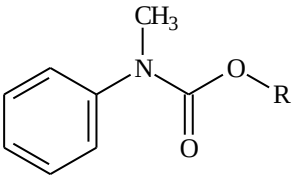
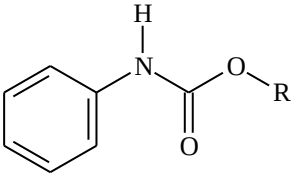
MW = 93.1 g mol^{-1}
T_m = -6.3 °C
C_w^{sat}(25°C) = 3.9 x 10^{-1} mol L^{-1}
K_{ow} = 7.9

10. A spill of methylparathion into a 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 was 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}



11. The rate constants obtained from the hydrolysis of a series of carbamates, where the R substituent was varied, produced the following LFER's with the pK_a of the conjugate acid of the leaving group.

(A)		$\log k_B = -0.25\ pK_a - 0.13$
(B)		$\log k_B = -1.15\ pK_a - 13.6$

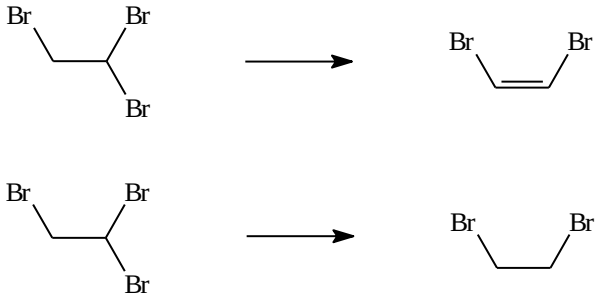
i) Explain the implications of observing two different correlations for 1° and 2° carbamates.
ii) Provide the mechanism of the base catalysed hydrolysis of (A)
iii) Explain the implications of the slope (including the negative sign) of the LFER in (A).
iv) Provide the mechanism of the base catalysed hydrolysis of (B)
v) Explain the implications of the slope (including the negative sign) of the LFER in (B).

12. The following data on 2-chlorophenol is available in the CRC Handbook of Chemistry and Physics: normal melting point (T_m) 9.0°C, normal boiling point (T_b) 174.9°C and the enthalpy of fusion, $\Delta H°_{fus}$ 12.52 kJ.mol^{-1} at 25°C.

Temperature, T (°C)	Vapor Pressure, P^o (kPa)
25.0	0.308

(i) calculate the enthalpy of vaporization, $\Delta H°_{vap}$ of 2-chlorophenol at 25°C
(ii) calculate the P°(L) of 2-chlorophenol at 5.0°C.
(iii) estimate the P°(s) of 2-chlorophenol at 5.0°C

13. a) Demonstrate, by calculating the oxidation states on carbon, whether the following reactions are reductions. For those reactions that are reductions provide the balanced half-reaction.



b) Explain the factors that may be involved in the rate determining step in a one electron transfer process.

c) Rationalize the increasing rate constants for the series: DC, DB, DI

Rates of disappearance of some halogenated ethanes in an anaerobic sediment-water slurry

Compound Name		Structure	k_{obs} (s^{-1})
1,2-dichloroethane	DC	CH_2Cl-CH_2Cl	$<<2 \times 10^{-7}$
1,2-dibromoethane	DB	CH_2Br-CH_2Br	3.5×10^{-6}
1,2-diiodoethane	DI	CH_2I-CH_2I	4.8×10^{-4}

14. Indicate the major product/s for each of the following reactions indicating where in the environment each of these transformations is likely to occur.