**1.*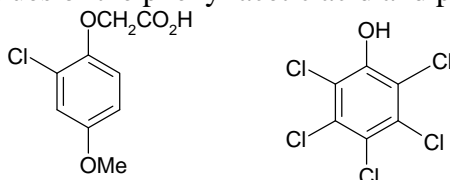* a) Interpret the following σ values in terms of the electronic character of each group. Indicate inductive and resonance contributions where appropriate, using substituted benzoic acids to illustrate your answer. [4]

Substituent	σ_{meta}	σ_{para}
-Cl	0.37	0.23
-COCH$_3$	0.36	0.47

b) Estimate the pK$_a$ values of the phenyl acetic acid and phenol derivatives below. [3]


c) Predict how the value of K$_{ow}$ for pentachlorophenol will vary with increasing pH. [2]

2. a) The hydrolysis of a series of ethyl benzoates by hydroxide ion in 85% aqueous ethanol has been investigated. A Hammett plot of the second order rate constants (k$_B$) gave a reaction constant ρ = 2.56. Calculate how much faster ethyl 4-nitrobenzoate will undergo base catalyzed hydrolysis compared to ethyl benzoate under similar conditions. [3]
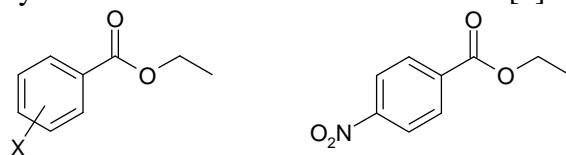

b) The hydrolysis of benzoyl chloride to give benzoic acid could proceed by two possible mechanisms shown below. A Hammett plot for substituted benzoyl chlorides gave a ρ = 0.8.
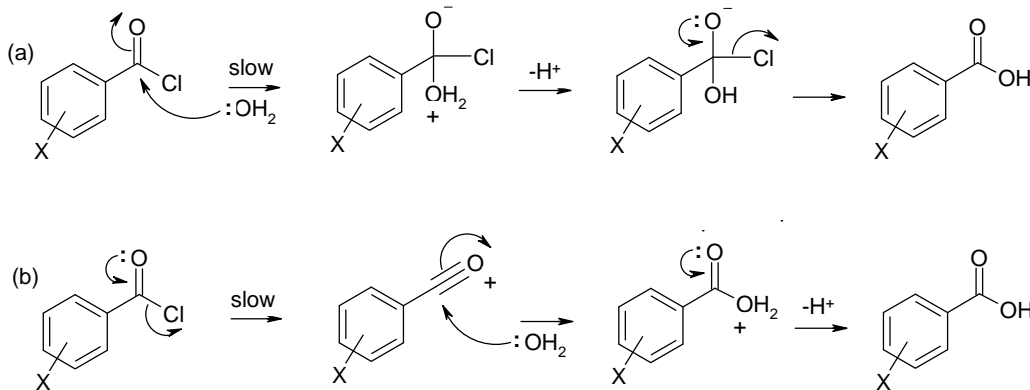

Which of the two mechanisms does the data support? Give reasons. [2]
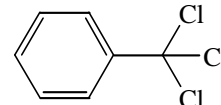Which of the two mechanisms would you expect to correlate with σ+ for a *para* methoxy substituent? [2]

3. 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. [5]
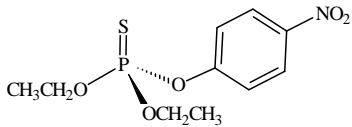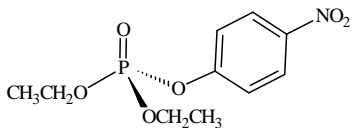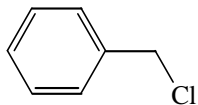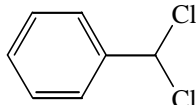
| Half-life | 15 hrs | 6 min | 19 s |

4. a) Provide the *stepwise* mechanism for **ONE** of the following **TWO** reactions indicating the rate determining step. [4]
   i) the base catalyzed hydrolysis of 2,4-dinitrophenyl acetate
   ii) the acid catalyzed hydrolysis of N-methylethanamide

b) Using the rate constant information provided below, sketch a log k_h vs pH profile for either 2,4-dinitrophenyl acetate **OR** N-methylethanamide. [4]

| Pollutant	k_A ($M^{-1}.s^{-1}$)	k_N (s^{-1})	k_B ($M^{-1}.s^{-1}$)
(2,4-dinitrophenyl acetate structure with NO$_2$ groups)	NI	1.1×10^{-5}	94
(N-methylethanamide structure, H$_3$C–C(=O)–N(H)–CH$_3$)	3.2×10^{-7}	NI	5.5×10^{-6}

NI = not important

5. From the information provided below at 25°C.
a) Provide the mechanism for the neutral hydrolysis of parathion. [2]
b) Calculate the half-life (in days) for abiotic hydrolysis of parathion at pH 8 and 25°C. [2]
c) Calculate the pH at which the rates of hydrolysis for the base catalyzed and neutral mechanisms of parathion are equal. [2]
d) Provide a rationale for why the k_B for parathion is less than the k_B for paraoxon. [2]
e) Provide the major product/s for the base catalyzed hydrolysis of paraoxon. [2]

Pollutant	k_A ($M^{-1}.s^{-1}$)	k_N (s^{-1})	k_B ($M^{-1}.s^{-1}$)
Parathion	NI	8.3×10^{-8}	5.7×10^{-2}
Paraoxon	NI	7.3×10^{-8}	0.39

NI = not important

6. Ten kilograms (10.0 kg) of 4-methylphenyl N-methyl carbamate is spilled into a lake during the month of April, pH 8 and 5°C (note: at 5°C, $pK_w = 14.73$).
a) Calculate the amount (in kg) eliminated 90 days later by abiotic hydrolysis. Acid catalysis of carbamates can be neglected while the neutral reaction may be significant. Assume at pH 12 the dominant mechanism is base catalysis. [10]
b) Indicate the base catalyzed hydrolysis products. [2]
c) Show the E1cb mechanism for the hydrolysis of 1° carbamates. [2 bonus]
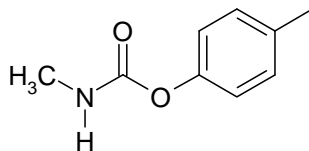
The following rate constant data was found in the literature.

Temperature (°C)	k_{hyd} (s^{-1})		
	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}