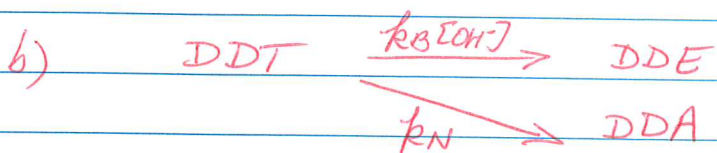


E2 = elimination, bimolecular

\therefore one concerted step w/ bond breaking & making simultaneous



@ $\text{pH} = 8.0$ $\text{pOH} = 14.53 - 8.0$ at 10°C
 $\therefore [\text{OH}^-] = 10^{-6.53} \text{ M}$

and $k_B[\text{OH}^-] = 5.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} (10^{-6.53} \text{ M}) = 1.47 \times 10^{-9} \text{ s}^{-1}$

$\therefore \%$ DDE = $\frac{k_B[\text{OH}^-]}{k_B[\text{OH}^-] + k_N}$
 non-reducing
 conditions

$$= \frac{1.47 \times 10^{-9} \text{ s}^{-1}}{2.47 \times 10^{-9} \text{ s}^{-1}} = 0.597$$

or 60%

$$2 a) \log \left\{ \frac{K_a(x)}{K_a(H)} \right\} = \rho \Sigma \sigma$$

$$\log K_a(x) - \log K_a(H) = \rho \Sigma \sigma$$

$$-\rho K_a(x) + \rho K_a(H) = \rho \Sigma \sigma$$

$$\therefore \rho K_a(x) = \rho K_a(H) - \rho \Sigma \sigma$$

$$\begin{aligned} \text{for PCB} &= 9.92 - 2.25 \left(\underset{\substack{\uparrow \\ 0.06}}{\sigma_m \text{ Ph}} + \underset{\substack{\uparrow \\ 0.23}}{\sigma_p \text{ Cl}} + \underset{\substack{\uparrow \\ 0.68}}{\sigma_o \text{ Cl}^{\text{phenol}}} \right) \\ &= 9.92 - 2.25(0.97) \\ &= 7.738 \end{aligned}$$

b)

$$\alpha_{HA} = \frac{[HA]}{[HA] + [A^-]} = \frac{1}{1 + 10^{(pH - pK_a)}}$$

$$= \frac{1}{1 + 10^{(7.41 - 7.738)}}$$

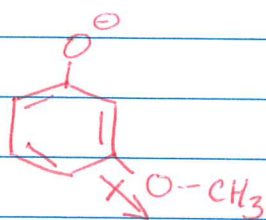
$$= \frac{1}{1.470} = 0.68$$



electron withdrawing by inductive effects
because oxygen is more electronegative than carbon
 $\therefore \sigma_I > 0$

electron donating by resonance effects
because lone pair electrons on oxygen can be delocalized through resonance to π -system
 $\therefore \sigma_R < 0$

$$\sigma_m \approx \sigma_I = 0.12$$

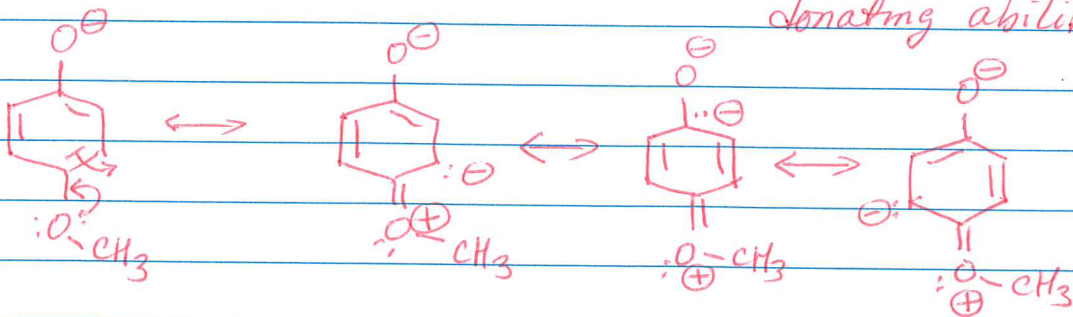


positive value consistent with
electron withdrawing in this
position

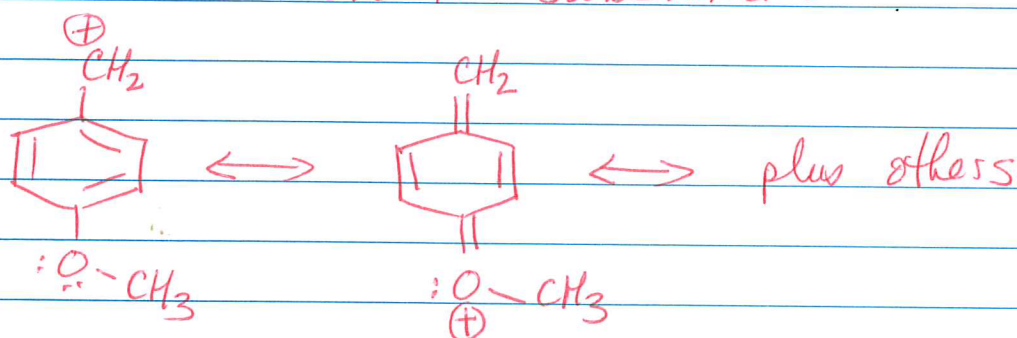
$$\sigma_p \approx \sigma_I + \sigma_R = -0.27$$

$$\therefore \sigma_R \approx -0.27 - 0.12 = -0.39$$

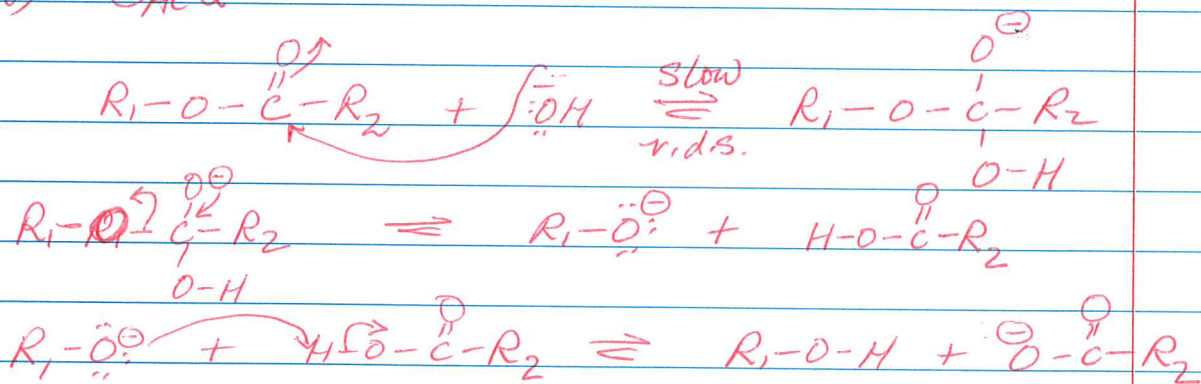
negative value
consistent with electron
donating ability in para



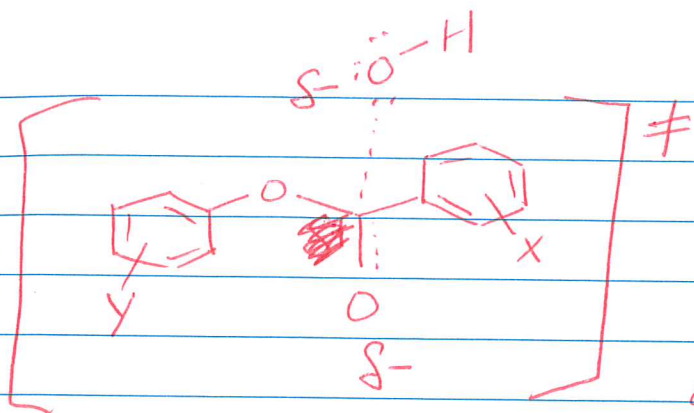
$\sigma^+ = -0.78$ modified substituent constant
 strongly electron donating when
 reaction centre has positive charge
 that can be resonance stabilized
 on to substituent



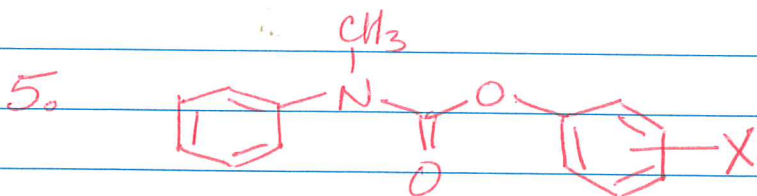
4. a) BAc2



b) $\rho > 0$ from substituents on either aromatic ring indicate the reaction kinetics are favoured by EWG. However, the magnitude of $\rho_x = 2.2$ versus $\rho_y = 1.1$ indicates that the energy of the transition step of r.d.s. is more stabilized by EWG's on aromatic directly attached to the carbonyl reaction centre versus the phenyl ring attached via oxygen.



substituents at X
have greater influence
on stabilizing build
up of electron density
at reaction centre.



what 'X' will
yield $t_{1/2} \sim 200$ days

$$k_B = 1.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} \quad [\text{OH}^-] = 10^{-6.00} \text{ M}$$

$$\therefore k_h \cong k_B [\text{OH}^-] = (1.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}) (10^{-6.00} \text{ M})$$

$$= 1.0 \times 10^{-10} \text{ s}^{-1}$$

$$k_{1/2} = \frac{0.693}{k_h} = 6.93 \times 10^9 \text{ s} \Rightarrow 8.0 \times 10^4 \text{ days}$$

~~What is the~~ Since $\rho = 1.3$, rate will be enhanced
by EWG (ie. $\sigma > 0$)

For $t_{1/2} = 200 \text{ d}$, we need $k_h = \frac{0.693}{200 \text{ d} \times \frac{24 \text{ h}}{\text{d}} \times \frac{3600 \text{ s}}{\text{hr}}}$

$$k_h = 4.0 \times 10^{-8} \text{ s}^{-1}$$

and therefore $k_B = \frac{k_h}{[\text{OH}^-]} = 0.040 \text{ M}^{-1} \text{ s}^{-1}$

$$\log \left\{ \frac{R_B(X)}{R_B(H)} \right\} = 1.3 \Sigma \sigma$$

$$\log \left(\frac{0.0401}{0.00010} \right) = 1.3 \Sigma \sigma$$

$$\therefore \Sigma \sigma = \frac{\log ({}^{10^4} 401)}{1.3} = 2.00$$

$$\sigma_m(\text{NO}_2) = 0.71$$

$$\sigma_m(\text{CN}) = 0.56$$

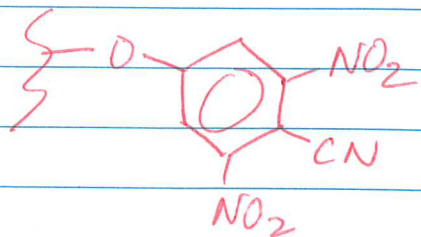
$$\sigma_p(\text{NO}_2) = 0.78$$

$$\sigma_p(\text{CN}) = 0.66$$

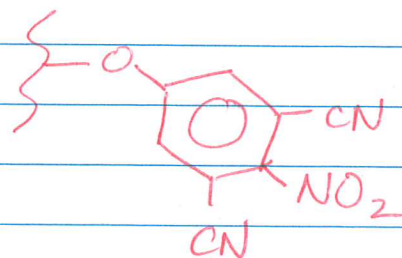
$$\Sigma \sigma = 2 \times \sigma_m(\text{NO}_2) + 1 \sigma_p(\text{CN}) = 2.08$$

OR

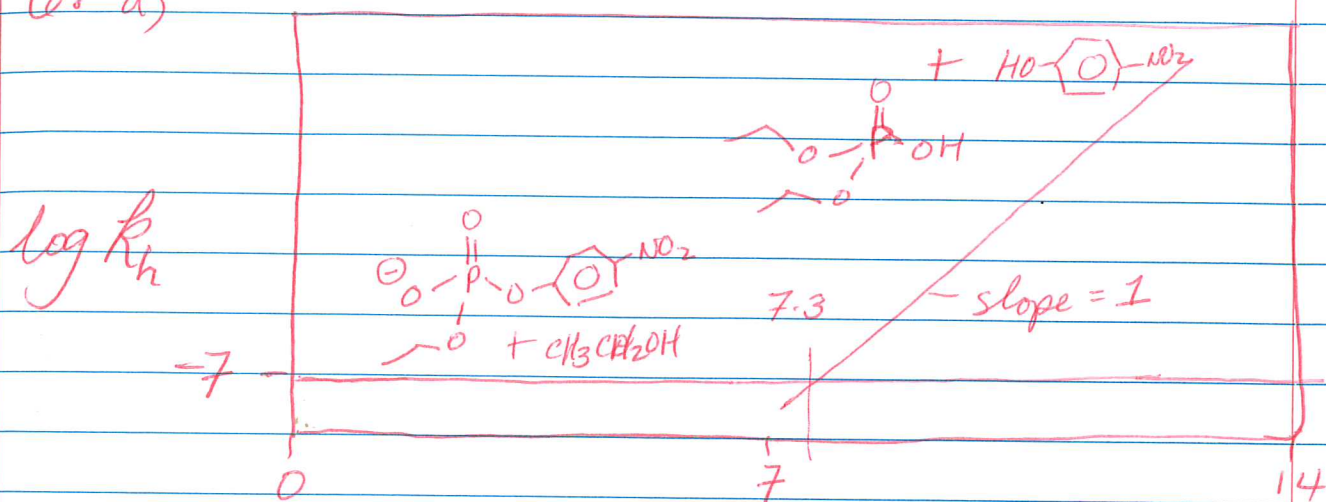
$$\Sigma \sigma = 2 \times \sigma_m(\text{CN}) + 1 \sigma_p(\text{NO}_2) = 1.90$$



OR



(e. a)



$$7.3 \times 10^{-8} \text{ s}^{-1} = 0.39 \text{ M}^{-1} \text{ s}^{-1} [\text{OH}^-]$$

$$\therefore [\text{OH}^-] = \frac{7.3 \times 10^{-8} \text{ s}^{-1}}{0.39 \text{ M}^{-1} \text{ s}^{-1}} = 1.87 \times 10^{-7} \text{ M}$$

$$\therefore \text{pOH} = 6.73 \quad \text{and} \quad \text{pH} = 14.00 - 6.73 = 7.27$$

b) $k_{\text{HS}^-} = k_{\text{H}_2\text{O}} 10^{nS}$, where $S=1$ and $n=5.1$

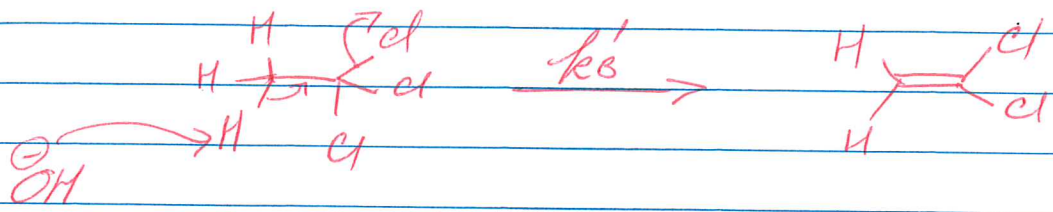
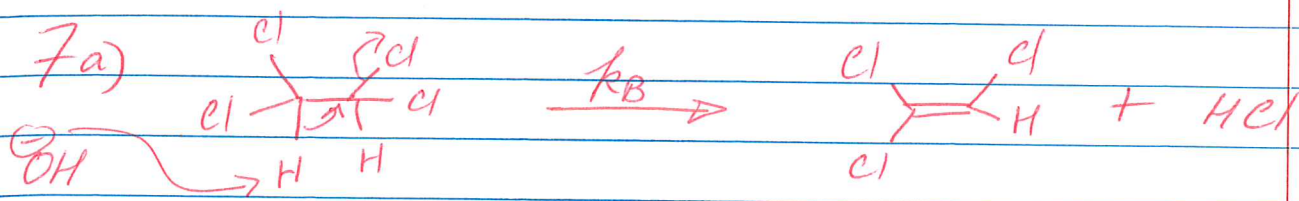
since $k_{\text{N}} = k_{\text{H}_2\text{O}} [\text{H}_2\text{O}] = 7.3 \times 10^{-8} \text{ s}^{-1}$

~~and $k_{\text{HS}^-} = k_{\text{H}_2\text{O}} 10^{5.1}$~~ $\therefore k_{\text{H}_2\text{O}} = \frac{7.3 \times 10^{-8} \text{ s}^{-1}}{55.5 \text{ M}} = 1.315 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$

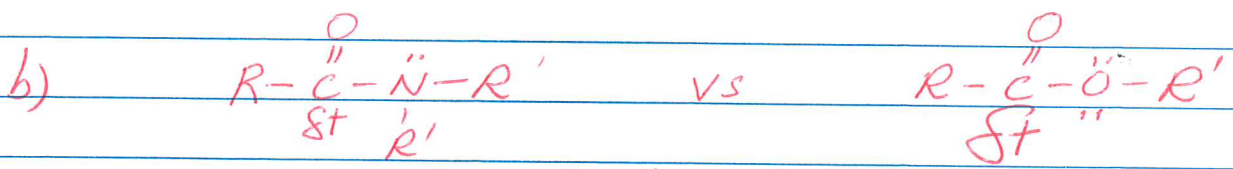
$$\therefore k_{\text{HS}^-} = 1.315 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1} \cdot 10^{5.1} = 1.656 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

To compete w H_2O , $k_{\text{HS}^-} [\text{HS}^-] \geq k_{\text{N}}$

$$\therefore [\text{HS}^-] = \frac{7.3 \times 10^{-8} \text{ s}^{-1}}{1.656 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}} = 4.41 \times 10^{-4} \text{ M} \quad \text{or} \quad 0.44 \text{ mM}$$



$k_B \gg k'_B$ because β -hydrogen of 1,1,2,2-tetrachloroethane is more acidic due to inductive EW effect of Cl atoms



amides less reactive to hydrolysis as carbonyl carbon is less electrophilic than that on ester, due to smaller electronegativity difference and greater resonance donation from nitrogen atom.

