Advanced Organic Chemistry certificate course 2021
Physical Organic Chemistry
Tutorial 1

1. Consider the following substituent constants and answer each of the following in terms of the inductive and resonance electronic character of each group. Illustrate your answer showing resonance structures for substituted benzoic acids where appropriate.

Substituent	σ_{meta}	σ_{para}
-OH	0.13	-0.38
$-COCH_3$	0.38	0.50
$-C_6H_2(NO_2)_3$	0.43	0.41

(a) Why is σ meta for the hydroxyl group (-OH) positive, where as the value for σ Para is negative
(b) Why is the acetyl group(-COCH3) a more electron withdrawing in para vs meta position?
© Why does the picryl substituent –C6H2(NO2)3 have nearly the same electron withdrawing ability in both the meta and para position?

2. Write the standard Hammett equation and define the parameters.
3. What information can the rho value (ρ) provide in a Hammett plot?
4. Using the information in Table 1 and 2 (page 2), estimate the pKa values of the following compounds at 25°C. You may use the following equation to calculate the substituent constants for the disubstituted compounds.

$$\log\left(\frac{K_a^{(X)}}{K_a^{(H)}}\right) = \rho \Sigma \sigma$$

$$\therefore pK_a(X) = pK_a(H) - \rho \Sigma \sigma_x$$

a) 4- bromo benzoic acid,

(b)3-Cynobenzoic acid,

(c) 4-nitro phenol

d) 3,4-dinitrophenol

e) 2,4-dichlorophenoxy acetic acid

f) the conjugate acid of para-methylaniline

Table 1: Hammett constants for some common substituents

Substituent	σ_{meta}	σ_{para}	σ^-	σ^+	$\sigma_o^{phenols}$
CH_3	-0.07	-0.17		-0.31	-0.13
Ph (C_6H_5)	0.06	0.01			
Cl	0.37	0.23		0.11	0.68
Br	0.39	0.23	0.26	0.15	0.70
I	0.35	0.18		0.13	0.63
OH	0.10	-0.37		-0.92	
OCH_3	0.12	-0.27	-0.12	-0.78	0.0
NO_2	0.71	0.78	1.25	0.79	1.24
CN	0.56	0.66	0.89	0.66	
CO_2CH_3	0.33	0.45	0.66		
$OCOCH_3$	0.36	0.31			
NH_2	-0.16	-0.66		-1.3	
$N(CH_3)_2$	-0.15	-0.83			

Note: σ^- and σ^+ apply to *para* substituted groups only

Table 2: Reaction and acidity constants for aromatic acids in water at 25°C

Acid	ρ	pK_{aH}
Benzoic acid	1.00	4.19
Phenol	2.25	9.92
Phenoxy acetic acid	0.30	3.17
2-chlorophenoxy acetic acid	0.30	3.05
Conjugate acid of aniline	2.89	4.63

5. How much faster m=Br benzyl chloride will solvolyze in H_2O than will m-nitro benzyl chloride?