CHEM 331

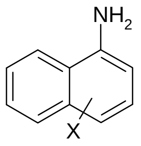
Problem Set #3: Substitutent Effects and LFERs

1. a) Interpret the following σ values in terms of the electronic character of each group. Discuss the inductive and resonance effects of each (σ_I and σ_R) using benzoic acid derivatives as examples, showing resonance where appropriate.

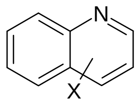
Substituent	σ_{meta}	σ_{para}
-OH	0.13	-0.38
$-COCH_3$	0.38	0.50
$-S(CH_3)_2^+$	1.0	0.90

b) The picryl (2,4,6-trinitrophenyl) substituent, $C_6H_2(NO_2)_3$ has values of σ_{meta} 0.43, σ_{para} 0.41. What conclusion may be drawn regarding the resonance effect of this substituent and the configuration of the two aromatic rings in 4-(2,4,6-trinitrophenyl)benzoic acid?

2. The pK_a's and reaction constants (susceptibility factors) ρ for the acid dissociation of substituted 1-naphthylamines and quinolines are given below.
a) Explain why the quinoline is much more susceptible to electronic substituent effects than 1-naphthylamine.
b) Predict the fraction of each compound present in the protonated form at pH = 6.00



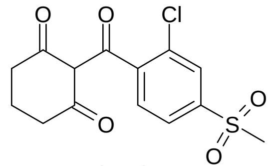
1-naphthylamine
$pK_a = 3.85$
$\rho = 2.81$



quinoline
$pK_a = 4.88$
$\rho = 5.90$

3. a) Estimate the pK_a values of 4-methyl-2,5-dinitrophenol and 3,4,5-trimethylaniline using the data given in Tables 1 and 2 (attached) at 25°C.

b) The structure of the herbicide *sulcotrion* is shown below and is found to have a pK_a of 3.13. Identify the acidic proton and explain the unusual acidity. Sketch a labeled plot of fractional abundance of the acid and basic forms over a pH range of 2 – 12.



sulcotrion

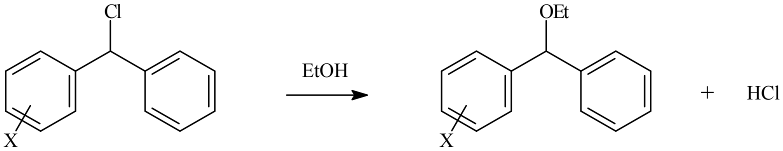
4. The pK_a values of m- and p-monosubstituted benzoic acids in 50% aqueous ethanol correlate with σ, and have a ρ value of 1.60. The pK_a of benzoic acid in this system is 5.71.The pK_a values of some 4-X-3,5-dimethylbenzoic acids in this medium are shown below. Use these results to examine and comment on the applicability of additivity of σ values.

X	$N(CH_3)_2$	NH_2	Cl	Br	CN	$COOCH_3$	NO_2
pK_a	6.23	6.88	5.59	5.55	4.90	5.44	4.91

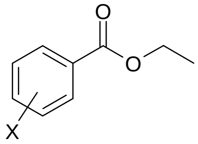
5. The relative rates of alkaline hydrolysis of substituted benzamides in water at 100°C are as follows below. Demonstrate the applicability of the Hammett equation to this reaction, calculate the ρ value, and comment on any deviations from the correlation.

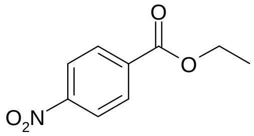
Substituent	Relative Rate	Substituent	Relative Rate	Substituent	Relative Rate
m-I	2.60	*m*-NO_2	5.60	*p*-OCH_3	0.49
p-I	1.69	H	1.00	*m*-NH_2	0.93
m-Br	2.97	*m*-CH_3	0.83	*p*-NH_2	0.20
p-Br	1.91	*p*-CH_3	0.65	*m*-OH	0.19

6. The solvolysis of substituted diphenylcarbinyl chlorides was studied in ethanol at 25°C. A plot of log *k* versus σ^+, displayed a linear correlation with a slope of −5.1. Suggest a mechanism that is consistent with this observation and provide an explanation of the sign and magnitude of the ρ value.

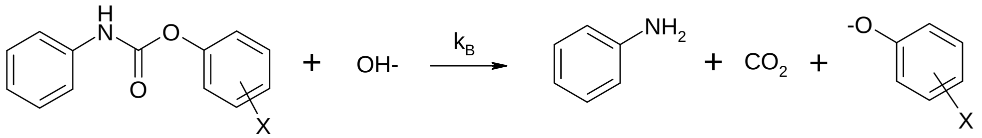


7. a) The hydrolysis of a series of ethyl benzoates by hydroxide ion in 85% aqueous ethanol has been investigated. A Hammett plot of the second order rate constants (k_B) gave a reaction constant ρ = 2.56. Calculate how much faster ethyl 4-nitrobenzoate will undergo base catalyzed hydrolysis compared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





b) The base catalyzed hydrolysis of phenyl N-phenyl carbamates occurs by the elimination of PhO^- group as the rate determining step. Estimate the second order rate constant, k_B for 3,4,5-trichlorophenyl N-phenyl carbamate at 25°C using the k_B values given in the Table below for other substituted phenyl N-phenyl carbamates and the Hammett relation.



$$\log\left\{\frac{k_B(X)}{k_B(H)}\right\} = \rho\Sigma\sigma_i$$

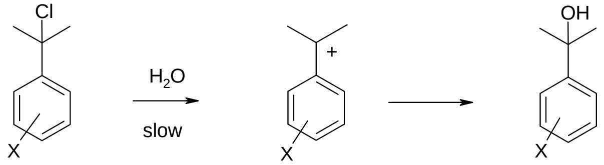
X	k_B (M^{-1} s^{-1})	X	k_B (M^{-1} s^{-1})
p-CH_3	3.0×10^1	*m*-Cl	1.8×10^3
p-OCH_3	2.5×10^1	*m*-NO_2	1.3×10^4
p-Cl	4.2×10^2	*p*-NO_2	2.7×10^5

8. For the following mechanisms:

a) Explain the value of the reaction (susceptibility) constant in terms of the Hammond postulate.

b) Specify which σ values are used (σ, σ^+, σ^-, or $\sigma_{ortho}^{phenols}$) in obtaining the susceptibility constant and indicate if the reaction centre is in direct resonance with the substituents. Illustrate with an example.

i) hydrolysis of substituted benzyl chlorides; $\rho = -4.45$



ii) addition of cyanide ion to substituted benzaldehydes; $\rho = 2.55$

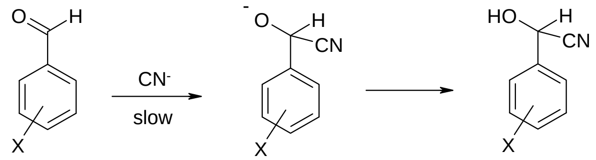


Table 1: Hammett constants for some common substituents

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