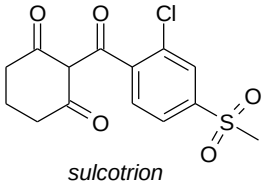
CHEM 331

Problem Set #3: Substitutent Effects and LFERs

Submit answers to <u>even numbered questions only</u>. Due Wednesday, Mar. 16th

1. The structure of the herbicide *sulcotrion* has is shown below and is found to have a pK_a of 3.13. Draw the structure of the conjugate base and explain the unusual acidity of this 'carbon acid'.



sulcotrion

2. Answer each of the following with reference to the corresponding substituent constants considering both inductive and resonance electronic contributions (σ_I and σ_R). Illustrate your answer showing resonance structures for substituted benzoic acids, where appropriate.

a) The σ_{meta} and σ_{para} values for the $-CO_2CH_3$ group are both positive with $\sigma_{para} > \sigma_{meta}$.

b) The values of σ_{meta} for the methoxy substituent ($-OCH_3$) is positive, whereas the values for σ_{para} is negative.

c) The picryl (2,4,6-trinitrophenyl) substituent, $-C_6H_2(NO_2)_3$ is relatively large with the ortho nitro groups sterically interfering with atoms in the ortho positions on an adjacent aromatic ring. Predict the sign and relative magnitude of σ_{meta} and σ_{para} for the picryl substituent.

3. Using the information in Table 1 and 2 (attached), estimate the pK_a values of the following compounds at 25°C and sketch a plot of the fractional abundance of each acid and conjugate base over a pH range of 0 – 14.

a) 3,4-dinitrophenol

b) 2,4-dichlorophenoxy acetic acid

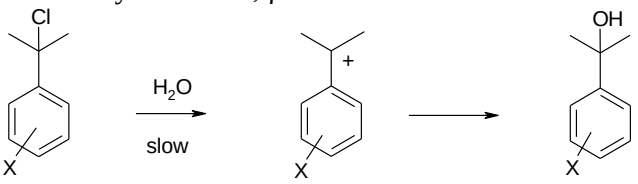
c) the conjugate acid of para-methylaniline

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 solvent system are given below. Use these results to examine and comment on the applicability of additivity of σ values.

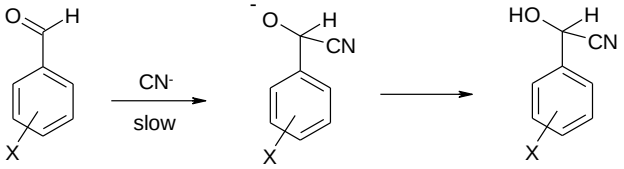
X	$N(CH_3)_2$	NH_2	Cl	Br	CN	$COOCH_3$	NO_2
pK_a	6.23	6.88	5.59	5.55	4.90	5.44	4.91

5. For each of the following mechanisms, indicate if the build up of charge at reaction centre is in direct resonance communication with substituents in the para position and specify which σ values would be used (σ, σ^+, σ^-, or $\sigma_{ortho}^{phenols}$) in obtaining the susceptibility constant. Illustrate your answer with an example.

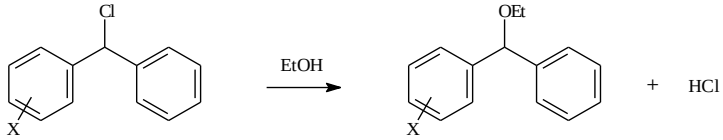
a) hydrolysis of substituted benzyl chlorides; ρ = –4.45



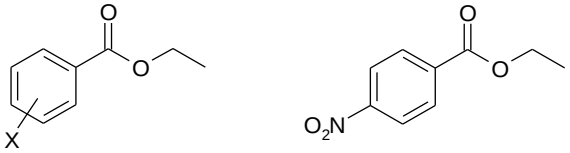
b) addition of cyanide ion to substituted benzaldehydes; ρ = 2.55



6. a) The solvolysis of substituted diphenylcarbinyl chlorides was studied in ethanol at 25°C. A plot of log *k* versus σ^+ was linear with a slope of –5.1. Suggest a mechanism consistent with this observation and provide an explanation of the ρ value in terms of the *Hammond postulate.*



b) 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.

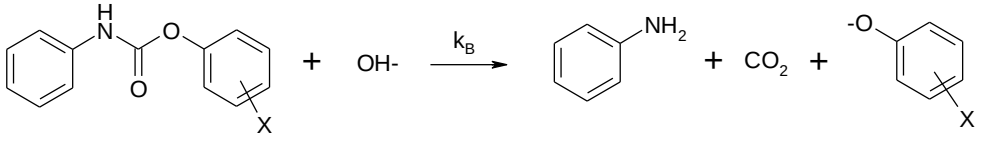


7. The neutral hydrolysis of 2,4-dinitrophenyl acetate (2,4-DNPA) has a measured pseudo first order rate constant of 4.4 x 10^{-5} s^{-1} at 22.5 °C.

a) If the reaction constant for a series of substituted phenyl acetates is determined to be ρ = 0.87, what is rate constant for the neutral hydrolysis of the unsubstituted phenyl acetate at this temperature.

b) Suggest a substituted phenyl acetate that will have a hydrolysis half-life greater than one week.

8. 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.



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

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 25ºC

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