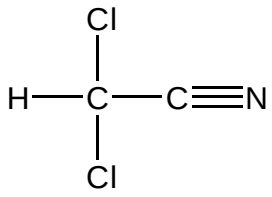
CEE 697K

Environmental Reaction Kinetics

Homework #4

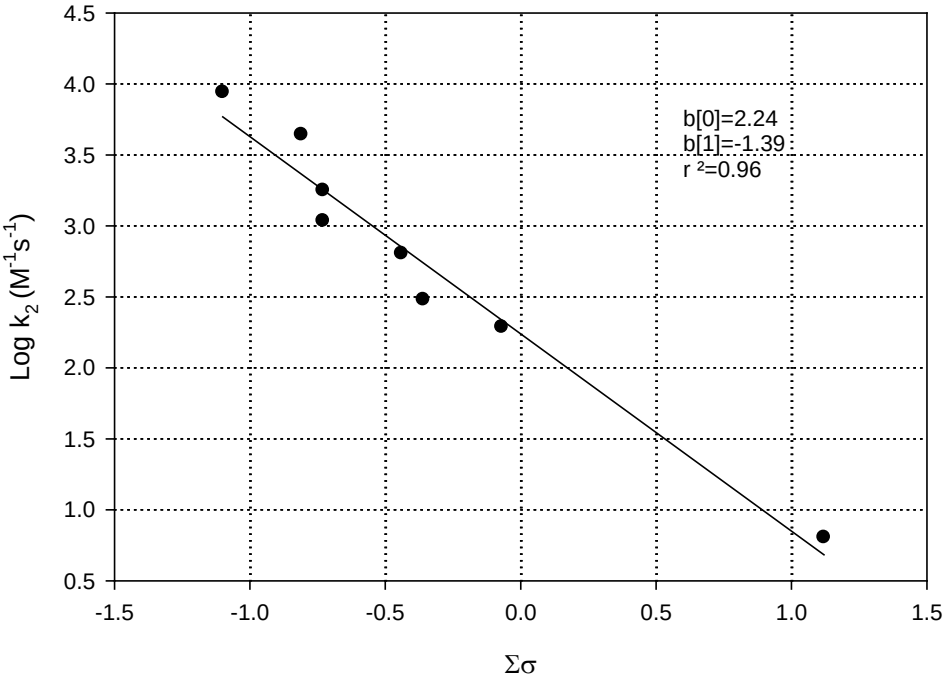
1. The data below are for the decomposition of Dichloroacetonitrile (DCAN) at pH 7, and 20 C. One column is for and ionic strength of 0.01 M (mostly NaCl), and the other for 0.03 M. Analyze these data and make any conclusions you can regarding the nature of the hydrolysis reaction of DCAN.

Time (hours)	DCAN Concentration (µg/L)	
	I = 0.01 M	I = 0.03 M
0.00	44.49	44.74
0.75	41.10	42.29
1.50	43.73	41.64
2.50	38.84	37.87
3.50	38.27	38.45
6.50	29.22	31.97
9.50	26.94	29.17
19.50	16.25	19.31
24.50	12.66	16.44
29.50	9.52	13.49
41.50	5.42	10.06
69.50	1.55	3.83
116.50		2.05



- Prepare 1st order and 2nd order graphs based on integral method
- Conclusion is that 1st order in DCAN fits best
- Rate constant goes up as ionic strength goes down
- Direction and magnitude of ionic strength effects implies that reaction is between a negative species (hydroxide) and a species with a positive center (maybe the carbon on the nitrile).

2. Prepare a Hammett Plot for the chlorination of phenol at high pH (i.e., phenate ions). Use all of the rate constants in Figure 13 from Deborde & von Gunten, 2008 [*Water Research* 42:13-51]. To help you with this you should number each carbon and treat the attack on different carbon atoms separately even if they result in the same product. Use the Hammett substituent constants in the attached table. Compare your results with those obtained by Deborde & von Gunten in their Figure 15.



Slope is much less than the one presented by Deborde & vonGunten.

3. Use the Hammett Plot prepared for #2, and predict the rate constant for the reaction of chlorine with the phenate ion of 2-amino-4-nitro-5-methyl phenol. Assume that the two unsubsituted carbons (C3 and C6) are the only sites of attack. Estimate the relative rate of attack on these two carbons.

2-amino-4-nitro-5-methyl phenol

	position	
	C3	C6
sigma	0.89	-0.67
log k	1.0029	3.1713
k	10.1	1483.5

$M^{-1}s^{-1}$

Therefore, the overall 2nd order rate constant is 1494 $M^{-1}s^{-1}$, or about 1.5 x10^3 $M^{-1}s^{-1}$, with slightly more than 99% of the attack at the #6 carbon.

Hammett Substituent Constants

Substituent	σ_p	σ_m	σ_o	σ_p+	$\sigma+_m$	σ^*	R	F
-$N(CH_3)_2$	-0.83	-0.16	-0.36	-1.70			-0.98	0.15
-O^-	-0.81	-0.47	-1.10					
-NH_2	-0.66	-0.15	0.03			0.10	-0.74	0.08
-OH	-0.35	0.08	0.04			0.25	-0.70	0.33
-OCH_3	-0.26	0.08	0.00	-0.76	0.05	0.25	-0.56	0.29
-$C(CH_3)_3$	-0.20	-0.10	-0.52	-0.26			-0.18	-0.02
-CH_3	-0.16	-0.07	-0.13	-0.31	-0.06	-0.05	-0.18	0.01
-$CH(CH_3)_2$	-0.15	-0.04	-0.23	-0.28			-0.19	0.04
-$CH_2C_6H_5$	-0.09	-0.08		-0.28			-0.05	-0.04
-$CH=CHC_6H_5$	-0.07	0.03		-1.00			-0.17	0.10
-$CH=CH_2$	-0.04	0.06		-0.16			-0.17	0.13
-OC_6H_5	-0.03	0.25		-0.50			-0.40	0.37
-C_6H_5	-0.01	0.06	0.00	-0.18	0.11	0.10	-0.13	0.12
-H	0	0	0	0	0	0	0	0
-$NHCOCH_3$	0.00	0.21		-0.60			-0.31	0.31
-CH_2OH	0.01	0.01	0.04					
-F	0.08	0.35	0.54	-0.07	0.35	0.52	-0.39	0.45
-Cl	0.23	0.37	0.68	0.11	0.40	0.47	-0.19	0.42
-Br	0.23	0.39	0.70	0.15	0.41	0.45	-0.22	0.45
-I	0.28	0.35	0.63	0.14	0.36	0.39	-0.24	0.42
-$CONH_2$	0.36	0.28	0.72				0.10	0.26
-CHO	0.42	0.35	0.75	0.73			0.09	0.33
-COC_6H_5	0.43	0.34		0.51			0.12	0.31
-$COOCH_3$	0.45	0.36		0.49			0.11	0.34
-$COCH_3$	0.50	0.38					0.17	0.33
-CN	0.68	0.62	1.32	0.66	0.56	0.58	0.15	0.51
-CH_3SO_2	0.71	0.65				0.59		
-NO_2	0.79	0.71	1.40	0.79	0.67	0.63	0.13	0.65

Note that σ_o values are estimated for phenols; source: Appendix A5 in Perrin, Dempsey & Serjeant, 1981, pKa Prediction for Organic Acids and Bases, Chapman & Hall.