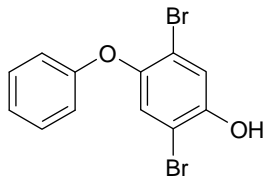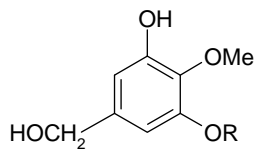# Example Problems

## *Applications of Hammett Equation: Substituent and Reaction Constants*

**1.** Predict the $pK_a$ for the following phenols using the appropriate substituent constants, a $pK_a$ for unsubstituted phenol of 9.90 and a $\rho$-value of 2.25.
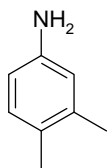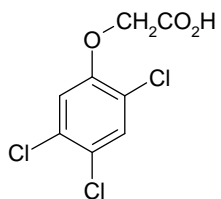


hydrolysis pdt of a PBDE



degradation pdt of gadusol

**2.** Predict the $pK_a$ of the following compounds and calculate the fraction present in ionized form at pH 6.00.
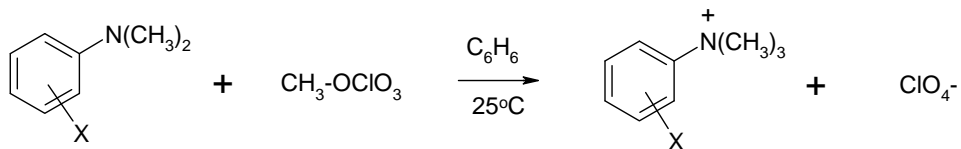
NH$_2$

O—CH$_2$CO$_2$H

Cl

Cl

Cl

3,4-DMA

2,4,5-T (herbicide)

|  | $pK_a$ | $\rho$ |
|---|---|---|
| aniline | 4.63 | 2.89 |
| 2-chlorophenoxyacetic acid | 3.05 | 0.30 |

**3.** Consider the substitution reaction and the kinetic data given below.



| Substituent (X) | $k$ (M$^{-1}$ s$^{-1}$) | Substituent (X) | $k$ (M$^{-1}$ s$^{-1}$) |
|---|---|---|---|
| 4-OCH$_3$ | 3.01 x 10$^{-2}$ | 4-Br | 6.12 x 10$^{-4}$ |
| 4-CH$_3$ | 1.12 x10$^{-2}$ | 3-Cl | 2.66 x 10$^{-4}$ |
| 3-CH$_3$ | 6.00 x 10$^{-3}$ | 3-NO$_2$ | 2.86 x 10$^{-5}$ |
| H | 3.44 x 10$^{-3}$ | 4-NO$_2$ | ? |

a) Comment on the use of $\sigma$ or $\sigma^+$ for this reaction.
b) Determine the reaction constant $\rho$ for this reaction and propose a mechanism.
c) Comment on the structure of the transition state.
d) Predict the rate constant for N,N-dimethyl *para*-nitroaniline (X = 4-NO$_2$)
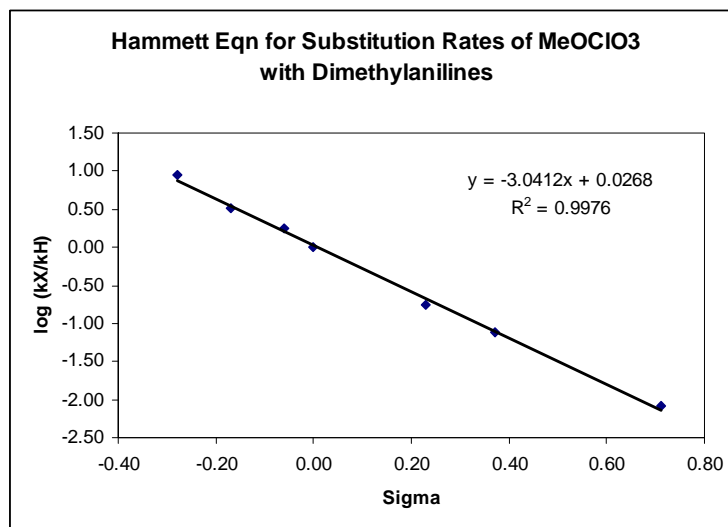
**4.** For the following Hammett plot and reaction below, two reaction (susceptibility) constants (ρ) are obtained, one for EDG and another for EWGs. Explain the magnitude and sign of each of the two reaction constants and provide mechanism/s consistent with these observations.





$\rho(\sigma^+) = -5.58$

$\rho(\sigma^+) = -2.81$

$\log\left\{\dfrac{k_X}{k_0}\right\}$

$\sigma^+$
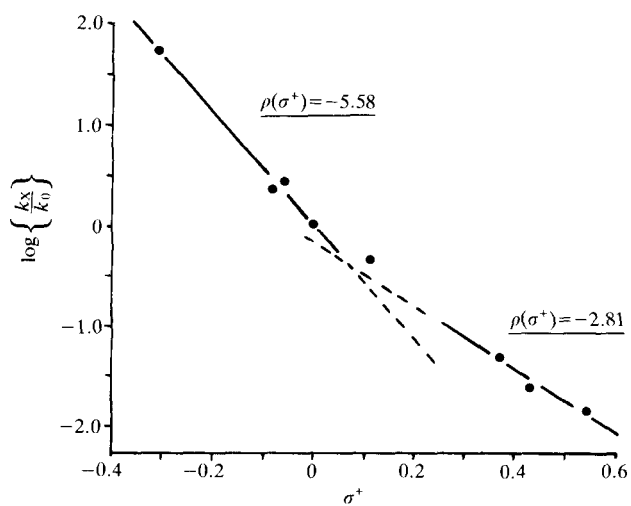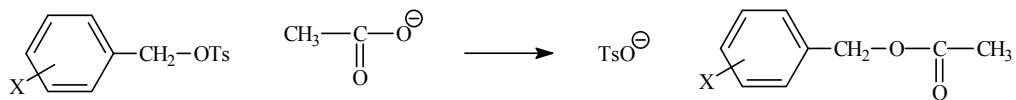
**5.** The following rate data are for the solvolysis of substituted benzyl azoxyarenesulfonates (I) at 25°C in aqueous trifluoroethanol.
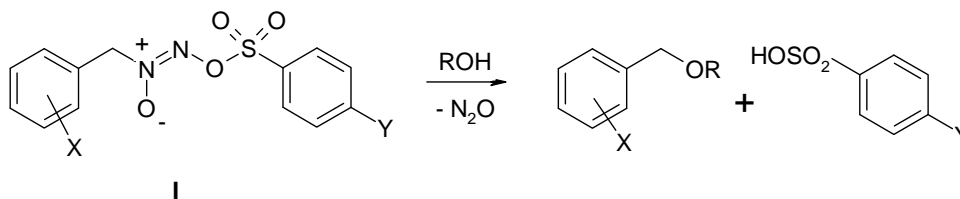


a) Calculate the reaction constants for the effects of substituents **X** and **Y** using the appropriate substituent constants.
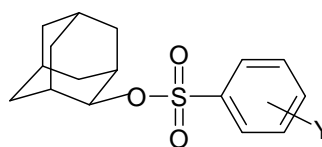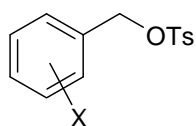
Table 1: Substituent Effects on Benzyl Ring

| X (for Y=CH₃) | $10^5 k$ (s⁻¹) |
|:---:|:---:|
| 3-Cl | 0.031 |
| 4-Cl | 0.23 |
| H | 0.47 |
| 3-CH₃ | 0.76 |
| 4-CH₃ | 6.0 |
| 4-OCH₃ | 170 |

Table 2: Substituent Effects on the Arenesulfonate

| Y (for X=4-CH₃) | $k$ (s⁻¹) |
|:---:|:---:|
| OCH₃ | 4.24 |
| CH₃ | 6.0 |
| Br | 19.1 |
| CN | 46.5 |

b) Using the following information, what may be deduced from the ρ-values for the solvolysis of **I** regarding its mechanism?



II                                          III

For the $S_N1$ solvolysis of substituted benzyl tosylates (**II**), ρ (vs σ+) = -5.6 and for 2-adamantyl arenesulfonates (**III**), ρ (vs σ) = 1.9.

**Hammett Plot for Changing X in Cmpd I**

$y = -3.306x + 0.105$
$R^2 = 0.9719$

log (kX/kH)

sigma +



**Hammett Plot for Changing Y in Cmpd I**

$y = 1.0655x - 4.0394$
$R^2 = 0.9876$

log kX

sigma