

Fig. 35-1



Louis P. Hammett (1894 - 1987)

<http://books.nap.edu/html/biomems/lhammett.html>

## Experiment 35

# ACIDITY OF BENZOIC ACIDS: A LINEAR FREE ENERGY STUDY

### Text Topics

Acidity, linear free energy relationships.

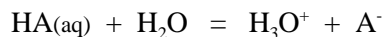
### Discussion

Inductive, resonance, steric, hybridization and hyperconjugation effects are used by organic chemists to explain and predict differences in properties and reactivity. *Exercise 6* asks you to apply these concepts to rank relative acidities of closely related compounds. Predicting how structural changes will affect properties and reactivity is challenging partially because structural changes usually impact more than one of the effects named above. It is difficult to control the variables and study only one of the effects. In addition, solvent effects, although often neglected, are also very important and very difficult to predict especially in a quantitative manner. Despite these pitfalls, in many closely related systems, substituents affect free energies and free energies of activation in a quantitative and sometimes linear fashion.

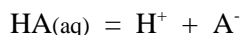
Louis P. Hammett was able to quantitatively relate relative equilibrium constants and reaction rates to parameters for substituents. Hammett obtained reasonably good fits for data to a linear free energy relationship [ $\log k/k_0 = \sigma\rho$ ] where  $k/k_0$  is the ratio of the reaction rate (or equilibrium constant) of a substituted compound to an unsubstituted (or parent) compound,  $\sigma$  (sigma) is a substituent constant and  $\rho$  (rho) is a reaction or property constant. The advantage of this approach is that tables of  $\sigma$  and  $\rho$  should be compilable and then used to predict properties and reactivity for previously untested compounds. While it turns out that this is a powerful technique, it is limited to systems where variables are controlled. The method should be considered semi-empirical and is not directly derivable from basic concepts.

For this experiment, the  $pK_a$  values for substituted benzoic acids (the same system Hammett originally studied) will be measured. The  $pK_a$  values will be plotted versus literature values of  $\sigma$  to examine the fit of your data to the Hammett equation and to determine a value of  $\rho$  for the ionization of benzoic acids in 48% ethanol. Because the value of  $\rho$  is sensitive to the nature of the solvent, the same solvent must be used throughout these experiments. In addition, the values of  $\sigma$  will be used to evaluate the relative amounts of resonance and inductive effects that are operative for some substituents.

$pK_a$  measurements provide valuable information for substituent effect studies. For a monoprotic acid, the general reaction for ionization in aqueous solution is:



The equation above is often simplified to:



It is possible to show in dilute solutions that the concentrations of reactants and products are approximately related to an equilibrium constant by the equation:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{equation 35-1}$$

Notice from the equation that the greater the amount of ionization (or the stronger the acid), the larger the  $K_a$  value is. For strong acids such as hydrochloric acid, which are almost completely ionized,  $K_a$  values are typically between 1 and  $10^{10}$ . Acids of moderate strength such as phosphoric acid have  $K_a$  values between  $10^{-3}$  and 1. Weak acids such as acetic acid and the benzoic acids of this study have  $K_a$  values below  $10^{-3}$ . Compounds with  $K_a$  values below  $10^{-11}$  are usually not called acids although their acidic properties often still play a significant role in synthesis reactions.

Four different methods of determining  $\text{p}K_a$  values are described below.

1. For a weak acid, measurement of the pH of a solution of known concentration leads to a straightforward approximation of the  $K_a$  value. For a weak acid, the amount of ionization is small compared to the total concentration of the acid. Insertion of the initial concentration of the acid for  $[\text{HA}]$  (the final equilibrium concentration of  $\text{HA}$ ) simplifies the calculation. However, always check the completed calculations to be sure the assumption was justified. The pH is used to approximate  $[\text{H}^+]$  and  $[\text{A}^-]$ . For the pure acid, these two values are the same because each time an acid molecule ionizes, one hydrogen ion is produced and one anion is produced. You should be able to show that:

$$\text{p}K_a = 2 \text{pH} + \log[\text{HA}]$$

2. The  $K_a$  for a weak acid may be determined by making a buffer solution in which the concentrations of  $\text{HA}$  and  $\text{A}^-$  are very close to equal. Since their concentrations will not change significantly as a result of ionization, their concentrations in *equation 35-1* cancel leaving  $K_a = [\text{H}^+]$ . Thus the measured  $\text{pH} = \text{p}K_a$

3. Many ions react with water in what is called a hydrolysis reaction. The most commonly encountered compounds that undergo hydrolysis are the salts of weak acids such as sodium acetate. Sodium acetate completely ionizes when dissolved in water but simultaneously a small fraction of the acetate ions react with water as in the reaction below with  $\text{A}^-$  representing the acetate.



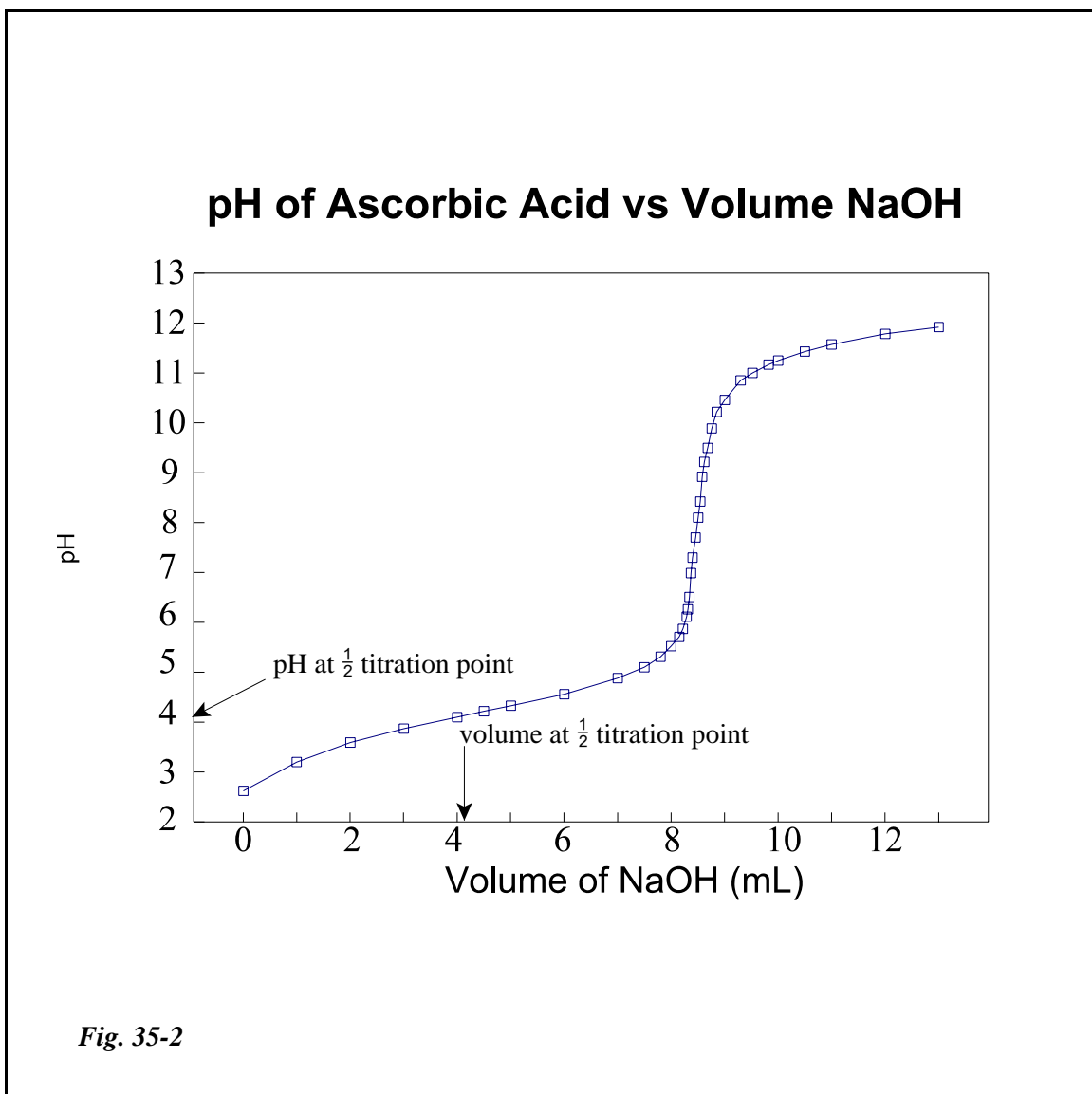
The equilibrium constants for hydrolysis are generally very small but it takes only tiny amounts of hydroxide for the pH to be significantly changed. Remember that in a neutral solution the hydrogen and hydroxide ion concentrations have the minuscule values of  $1 \times 10^{-7}$  M. Any reaction that produces even small amounts of hydrogen or hydroxide ions will affect the very sensitive pH measurement. Because of hydrolysis, ions such as acetate, carbonate and phosphate commonly make their aqueous solutions basic. The equilibrium constant expression for the hydrolysis reaction above is:

$$K_H = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{[\text{HA}][\text{OH}^-][\text{H}^+]}{[\text{A}^-][\text{H}^+]} = \frac{K_w}{K_a}$$

In the second step above, both the numerator and denominator have been multiplied by  $[\text{H}^+]$ . By careful inspection, we notice that the hydrolysis constant  $K_H$  is equal to  $K_w/K_a$  and  $K_a = K_w/K_H$ . If the pH is measured for a solution of known concentration of a salt (such as sodium acetate), the  $[\text{OH}^-]$  can be calculated by using

the relationship  $\text{pH} + \text{pOH} = 14$  and taking the antilogarithm of the negative of the result. According to the hydrolysis reaction, for every hydroxide produced, there will also be one HA produced thus the hydroxide concentration is the same as the HA concentration. As the amount of hydrolysis of  $\text{A}^-$  is very low, the original concentration of  $\text{A}^-$  can be inserted into the expression for  $K_{\text{H}}$  and the value for  $K_{\text{H}}$  can now be calculated. Finally  $K_{\text{a}}$  is  $10^{-14}/K_{\text{H}}$ .

4. A fourth method you will have available to determine  $K_{\text{a}}$  for the benzoic acids is more complex and involves the determination of a titration curve. Basically, the titration curve is produced by taking pH measurements at small intervals throughout the neutralization of the benzoic acid by sodium hydroxide. The equivalence point will be easily obtainable by inspection of a graph of pH vs the volume of NaOH solution added. At the half equivalence point (divide the volume of NaOH used to reach the equivalence point by 2), the concentration of HA will be very close to the concentration of  $\text{A}^-$  as half of the HA will have been neutralized or converted to product. At this point, as with the buffer solution described in #2, the concentrations of HA and  $\text{A}^-$  cancel and  $K_{\text{a}}$  is equal to  $[\text{H}^+]$ . Thus the pH at the half titration point should be a good value for  $\text{p}K_{\text{a}}$ .



## Techniques

Because there are significant solvent effects on benzoic acid  $pK_a$  values, the solvent for all procedures should be prepared in the same way by mixing equal volumes of 95% ethanol and water to give 48% ethanol solutions.

## Procedure

Choose one of the four methods for determining  $K_a$  values from those given in the Discussion section. Although the best one is probably the fourth or titration curve method, titration curves require considerably more time to determine than the other methods. If the titration method is selected, a group approach to this experiment should probably be used with each group doing titration curves for one or two of the substituted benzoic acids. The results should then be shared with the other groups. For quicker measurements, method 2 is recommended. Even for this method, considerable time and resources are saved if a group approach is used. More detailed instructions for method 2 are in the next paragraph.

A standardized 0.010 M NaOH solution in 48% ethanol will be provided. Weigh into a 25 mL volumetric flask, the calculated amount of the assigned benzoic acid to give twice the number of moles of the acid as the number of moles of sodium hydroxide that will be added (about  $2.5 \times 10^{-4}$  moles depending on the exact concentration of sodium hydroxide). Dissolve and fill to the mark with the sodium hydroxide solution. Measure the pH of the solution at a specified temperature and calculate the  $K_a$  for the acid.

## Calculations

According to the Hammett equation,  $\log k/k_o = \sigma\rho$ , a graph of  $\log K_a$  vs  $\sigma$  should give a straight line with slope  $\rho$  and an intercept of  $\log K_{\text{benzoic acid}}$ . Plot the graph for the data available and answer the questions below.

Table of  $\sigma$  values

Substituent	$\sigma_m$	$\sigma_p$
none (-H)	0.00	0.00
-CH <sub>3</sub>	-0.07	-0.17
- <i>t</i> -butyl		-0.20
-OCH <sub>3</sub>	0.12	-0.27
-F	0.34	0.06
-Cl	0.37	0.23
-Br	0.39	0.23
-NO <sub>2</sub>	0.71	0.78
-NHCOCH <sub>3</sub>		0.00
-CHO*	0.35	0.42
-COCH <sub>3</sub> *	0.38	0.50
-CN*	0.56	0.66
-CF <sub>3</sub> *	0.43	0.54

\*commercially available but expensive

## References

Hathaway, B. A.; Olessen, B. J. *Chem. Ed.*, **1993**, *70*, 953-955.

Brieger, G. *A Laboratory Manual for Modern Organic Chemistry*, Harper & Row, **1969**, p 129.

Isaacs, N. S. *Experiments in Physical Organic Chemistry*, Macmillan, **1969**, 8.

[http://www.wiredchemist.com/chemistry/data/hammett\\_sigma\\_constants.html](http://www.wiredchemist.com/chemistry/data/hammett_sigma_constants.html)

<http://old.iupac.org/publications/pac/1997/pdf/6912x2497.pdf>

## Prelaboratory Preparation - *Experiment 35*

First, be sure to list all the goals of the experiment. Explain why it is ok to abbreviate  $\text{H}_3\text{O}^+$  with  $\text{H}^+$ .

## Observations

Report all relevant observations including, masses and pH values.

## Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. Does a linear free energy relationship exist for this system (was the Hammett equation reasonably followed)?
3. Why is the substituent constant for methoxy positive in the meta position and negative in the para position. Comment on the magnitudes of the inductive and resonance effects of methoxy in each position.
4. To determine the values for  $\sigma$ , Hammett arbitrarily assigned a value to  $\rho$  for this system of unity. Did you obtain a value within experimental value of 1.0?
5. Why is the magnitude of  $\sigma$  for chlorine smaller in the para position than in the meta position?

