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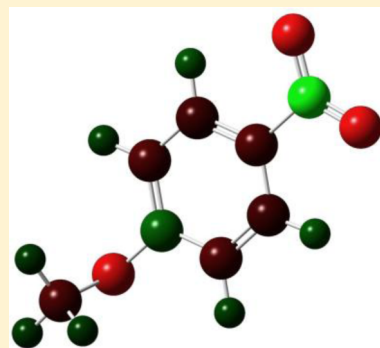
Theoretical Hammett Plot for the Gas-Phase Ionization of Benzoic Acid versus Phenol: A Computational Chemistry Lab Exercise

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S Supporting Information

ABSTRACT: Computational chemistry undergraduate laboratory courses are now part of the chemistry curriculum at many universities. However, there remains a lack of computational chemistry exercises available to instructors. This exercise is presented for students to develop skills using computational chemistry software while supplementing their knowledge of physical organic chemistry, specifically Hammett plots. Students use quantum calculations to determine the gas-phase Gibbs energy of ionization of substituted benzoic acids and phenols to generate a theoretical Hammett plot, thereby familiarizing themselves with the application of computational chemistry to physical organic chemistry.



KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Laboratory Instruction, Computer-Based Learning, Hands-On Learning/Manipulatives, Acids/Bases, Computational Chemistry, Thermodynamics

Computational chemistry is becoming an increasingly important tool for chemists. A quick search of the term “computational chemistry” using Thomson Reuters Web of Science shows an almost exponential increase in the amount of published items related to this search term since 1993. Due to the increasing application of this field in many areas of chemistry, it would be prudent to ensure undergraduate chemistry students are receiving an adequate background. To this end, many universities are now offering computational laboratory courses to undergraduate chemistry students. Aiding in this effort, a number of computational chemistry lab exercises have been published in recent years. The topics of these exercises include molecular geometry optimizations (bond length and angles), energetics, molecular and atomic orbital determination, transition states, and vibrational frequency analysis.^{1–6} These basic computational techniques have also been applied in undergraduate laboratory settings, as published in this *Journal*, to familiarize students with phenomena such as the Diels–Alder reaction,⁷ the decomposition of carbene hydroxymethylene,⁸ the potential energy surface of an argon dimer,⁴ the dissociation of alkyl halides,⁹ and the binding Gibbs energy of cyclodextrin-indole.¹⁰ Computational chemistry techniques have also been paired with wet-lab experiments to better familiarize students with fundamental physical chemistry.¹⁰

Hammett plots have long been an important topic in organic chemistry curricula due to their usefulness in relating structure and activity of molecules. This *Journal* has published many insightful articles on the topic of Hammett plots. Smith et al. reported an exercise in which a Hammett plot was used to demonstrate the effects of substituents on the esterification of

trifluoroacetic acid.¹¹ Marrs also developed an exercise to explore substituent effects on the ionization of phenols using a UV spectrometer.¹² In addition, Ikeda et al. reported an exercise in which a Hammett plot was used to probe the mechanism of semicarbazone formation.¹³ Also of note, Keenan et al. used a Hammett plot to enhance students’ understanding of substituent effects on the hydrolysis rates of *p*-nitrophenyl benzoate esters.¹⁴ As demonstrated in such reports, typical Hammett analyses compare the reaction rates or equilibrium constants for reactions of species with a phenyl ring that has varying substituents.

In the current work, theoretical values of the substituent constant, σ , are calculated at the HF/3-21G level of theory for the gas-phase ionization of benzoic acid (Scheme 1) at 298 K

$$\log \frac{K_X}{K_0} = \sigma$$

where K_0 is the equilibrium constant for the gas-phase ionization of benzoic acid and K_X is the equilibrium constant for the gas-phase ionization of a substituted benzoic acid. The subscript X represents the substituent. The substituent constant

Scheme 1. Reaction Studied in the Current Work

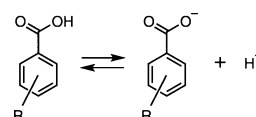


Table 1. Calculated and Experimental ΔG of Gas-Phase Ionization and Sigma Values for Benzoic Acids and Phenols at 298 K

Substituent (X)	Benzoic Acid				Phenol			
	$\Delta G_{298K}/(\text{kJ/mol})$ HF/3-21G	σ or $\text{Log}(K_X/K_0)$ HF/3-21G	$\Delta G_{298K}/(\text{kJ/mol})$ B3LYP/6-311++G**	Exp $\Delta G_{298K}^a/(\text{kJ/mol})$	$\Delta G_{298K}/(\text{kJ/mol})$ HF/3-21G	$\sigma\rho$ or $\text{Log}(K'_X/K'_0)$ HF/3-21G	$\Delta G_{298K}/(\text{kJ/mol})$ B3LYP/6-311++G**	Exp $\Delta G_{298K}^a/(\text{kJ/mol})$
<i>p</i> -NO ₂	1435.6	10.78	1363	1362	1398.4	23.35	1343	1343
<i>m</i> -NO ₂	1442.2	9.45	1369	1371	1463.1	12.00	1384	1386
<i>p</i> -Cl	1463.6	5.70	1398	1390	1482.2	8.65	1423	1424
<i>m</i> -Cl	1462.6	5.88	1395	1389	1484.4	8.27	1416	1418
H	1496.1	0.00	1417	1409	1531.6	0.00	1450	1451
<i>m</i> -OCH ₃	1484.8	1.99	1420	1407	1531.8	−0.02	1449	1445
<i>p</i> -OCH ₃	1500.8	−0.82	1427	1412	1536.1	−0.79	1454	1455
<i>m</i> -NH ₂	1503.0	−1.19	1424	1415	1548.5	−2.96	1457	1455
<i>p</i> -NH ₂	1518.9	−3.99	1436	1418	1567.3	−6.24	1466	1469

^aData for experimental values are from refs 16 and 17.

was calculated previously for the gas-phase ionization of benzoic acids.

Equilibrium constants, K_X and K_0 , can be calculated using the following equation

$$K = e^{-\Delta G/RT}$$

where K is the equilibrium constant for the ionization of benzoic acid, ΔG is the difference in Gibbs energy between products and reactants, R is the universal gas constant, 0.008314 kJ/(mol K), and T is the temperature, 298 K. The difference in Gibbs energy between products and reactants, ΔG , can be calculated from

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

where G_{products} is the Gibbs energy of the products, benzoic acid anion and $G_{\text{reactants}}$ is the Gibbs energy of the reactants, benzoic acid.

With the σ values calculated for the gas-phase ionization of benzoic acid, the Hammett equation can be applied to compare the gas-phase ionization of benzoic acid to that of phenol,

$$\log \frac{K'_X}{K'_0} = \sigma\rho$$

where K'_0 is the equilibrium constant for the gas-phase ionization of phenol at 298 K, and K'_X is the equilibrium constant for the gas-phase ionization of a substituted phenol. The subscript X represents the substituent. The σ represents the substituent constant as calculated previously for the gas-phase ionization of benzoic acids and ρ is the reaction constant. The ρ value represents the sensitivity of the reaction to substituent effects and is equal to the slope of a Hammett plot.

To the knowledge of the author, only Smith et al. have previously reported an exercise that combines Hammett phenomena with quantum calculations.¹¹ That study investigated the theoretical charge of the oxygen atom of substituted alcohols versus $\log(k/k_0)$, where k was the rate constant for the esterification of trifluoroacetic acid with substituted ethanols and k_0 was the rate constant for the esterification of trifluoroacetic acid with ethanol, using the AM1 semiempirical method to complement a wet-lab Hammett experiment. The current work introduces a novel computational laboratory exercise in which students develop a theoretical Hammett plot comparing the gas-phase ionization of benzoic acids and phenols to familiarize themselves with computational chemistry. The exercise complements courses introducing physical organic chemistry concepts.

EXPERIMENT

The Gaussian 09 suite of programs¹⁵ was used to carry out ab initio calculations on a Windows 7 OS laptop computer with an Intel Core i5–2540 M processor at 2.6 GHz and 6 GB of memory. Geometry optimization and frequency calculations were performed by students at the HF/3-21G level of theory, which allows adequate conveyance of the principles behind the exercise at low computational cost. However, where more sophisticated computational hardware is accessible, calculations may be performed at a higher level of theory. B3LYP/6-311++G** was chosen for the higher-level calculations for this study. Higher-level calculations may also be divided among students to prepare a collaborative theoretical Hammett plot where sufficient computational hardware is not accessible to individual students. The instructor may also complete higher-level B3LYP calculations in advance of the laboratory experiment for use as a comparison tool to student-completed lower-level HF calculations to aid students' understanding. The calculations performed, the results, and comparative experimental energetics are shown in Table 1.

HAZARDS

There are no hazards associated with this lab.

DISCUSSION

A theoretical Hammett plot for the gas-phase ionization of substituted phenols and benzoic acids was obtained at the HF/3-21G level. The Gibbs energy of the deprotonated anion and neutral for each substituted molecule was calculated for a total of 36 calculations. Each calculation required approximately 2 min of computational time allowing for this exercise to be completed easily in a 3-h laboratory period. The results of these calculations are shown in Table 1. As previously stated, this exercise may also be completed at the more accurate B3LYP/6-311++G** level by either students or in advance by instructors for comparison, data shown in Table 1, where the computational resources are available. Values calculated at this level of theory differ much less from experimental values compared to calculations at the HF/3-21G level. However, this report focuses on calculations carried out at the HF/3-21G level, as it is much less computationally demanding, and can be used to generate a Hammett plot which is adequate for explanation of observed chemical phenomena.

To begin, the electron-withdrawing group $-\text{NO}_2$ in the para-position is capable of stabilization through both induction and resonance. The ionization with $-\text{NO}_2$ at the meta-position is

roughly 7 kJ/mol less favorable for benzoic acid and roughly 63 kJ/mol less favorable for phenol compared to that of the para-position. This substantial energetic difference between the two acids arises because the negative charge of the phenoxide ion may be resonance delocalized into the ring and onto the *p*-nitro-group, whereas this possibility is substantially less favorable for the benzoate ion. Also, as the negative charge is further removed from the ring in the benzoate ion, the inductive effects of substituents are dampened. This phenomenon is also evident in the slope of the Hammett plot, or ρ value, of Figure 1.

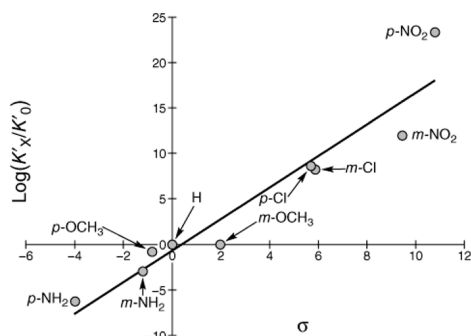


Figure 1. Theoretical Hammett plot of equilibrium constants for the gas-phase ionization of substituted benzoic acids and phenols at 298 K calculated at HF/3-21G: slope = 1.73, y -intercept = 0.65, and R^2 = 0.92.

The slope of the plot shown in Figure 1 is 1.73, that is, greater than 1, which suggests that the ionization of phenol is more sensitive than benzoic acid to substituent effects. This is the direct result of the ability of phenoxide ion to readily delocalize negative charge into the phenyl ring where the effects of the substituent are more significantly felt. If this value were lower than 1, the result would imply that the ionization would be less sensitive to substituent effects. It is interesting to note that if the point for *p*-NO₂ is removed from the linear correlation, the slope becomes 1.41 with a regression coefficient of 0.97 indicating that the *p*-NO₂ has an exceptional effect due to its ability to resonance delocalize charge. The sign of the slope is also relevant. Because it is positive, it implies that the ionization of phenol is favored by electron-withdrawing groups. This is due to the stabilization of the phenoxide anion by resonance and inductive effects by electron-withdrawing groups.

Relevant bond lengths and Mulliken charges may also be analyzed from Gaussian output files to aid in the understanding and explanation of substituent effects (Figure 2). It is of note that the gas-phase Gibbs energy of ionization values of *m*- and *p*-nitrobenzoates, whether determined by theoretical or experimental methods, are not dramatically different. This is also demonstrated by the negative charges on the carboxylate and nitro oxygens, which are comparable in both substituted molecules. Similarly, the C–N bond distances of the nitro substituents for both the meta- and para-species are not significantly different. In contrast, a comparison of *m*- and *p*-nitrophenolates shows a significantly shorter C–N bond distance in the para-substituted species, substantially greater negative charge on the nitro oxygens, and less negative charge on the oxide oxygen. As expected, there is also a relatively large difference in the gas-phase free energies of ionization of *m*- and *p*-nitrophenolates. As stated, this effect is a result of the ability

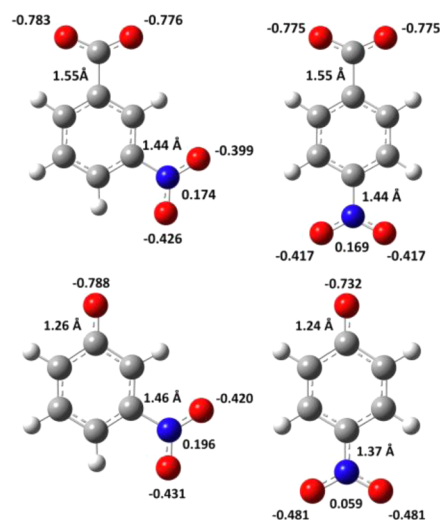


Figure 2. Structures of *m*- and *p*-nitro benzoates and phenolates with relevant bond lengths and Mulliken charges calculated at HF/3-21G.

of the negative oxide charge of the phenolate ion to be delocalized by resonance into the *p*-nitro group and not the *m*-nitro group.

The –Cl substituent is a weaker electron-withdrawing group and follows –NO₂ in the series. The para- and meta- ionization energies are reversed from the expected trend for both phenols and benzoic acids. This is believed to be a result of the inductive electron-withdrawing effects of chlorine in both positions but converse resonance electron-donating effects through *p*-type orbitals in the para- position of the neutral molecule. This leads to a stabilization of the neutral molecule and hence makes the molecule less acidic. The –H substituent is associated with a σ value of zero which is common to all Hammett plots. The gas-phase Gibbs energy of ionization of benzoic acid is approximately 36 kJ/mol more favorable than that of phenol.

The electron-donating groups such as –OCH₃ and –NH₂ are next in the series. The σ value of the *m*-OCH₃ group is positive, suggesting that the –OCH₃ group is electron withdrawing. However, it is important to remind students that this group is traditionally thought to be electron donating. This anomaly is thought to result from the ability of –OCH₃ to be inductively electron withdrawing in the meta-position because of the electronegativity of oxygen, and electron donating in the para-position through the lone electron pairs of oxygen and *p*-orbital overlap with that of the phenyl ring. The *p*-NH₂ group is the most electron-donating group, by resonance and induction, of the series for both benzoic acid and phenol. Particularly where the exercise may be completed in student groups, data for other substituents may be calculated and added to the theoretical Hammett plot to provide further examples of both resonance and inductive effects of electron-withdrawing and electron-donating groups. The substituents included in the experiment described herein have been chosen to illustrate prototypical substituent effects.

CONCLUSION

This exercise allows for students to gain practical experience with computational chemistry while also learning about a common topic in physical organic chemistry, Hammett plots. It can be easily completed during a typical 3-h lab period and synchronizes many fundamental themes in chemistry. The

theoretical Hammett plot generated from a series of Gibbs energy calculations of the gas-phase ionization of benzoic acids and phenols accurately parallels previous studies of Hammett plots, while maintaining low computational cost at the HF/3-21G level of theory. If computational resources are available, students may also complete calculations at the higher B3LYP/6-311++G* level of theory in order to compute chemically accurate energetics of the gas-phase ionization of phenols and benzoic acids.

■ ASSOCIATED CONTENT

■ Supporting Information

Student handout; questions for the students; notes for the instructor. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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