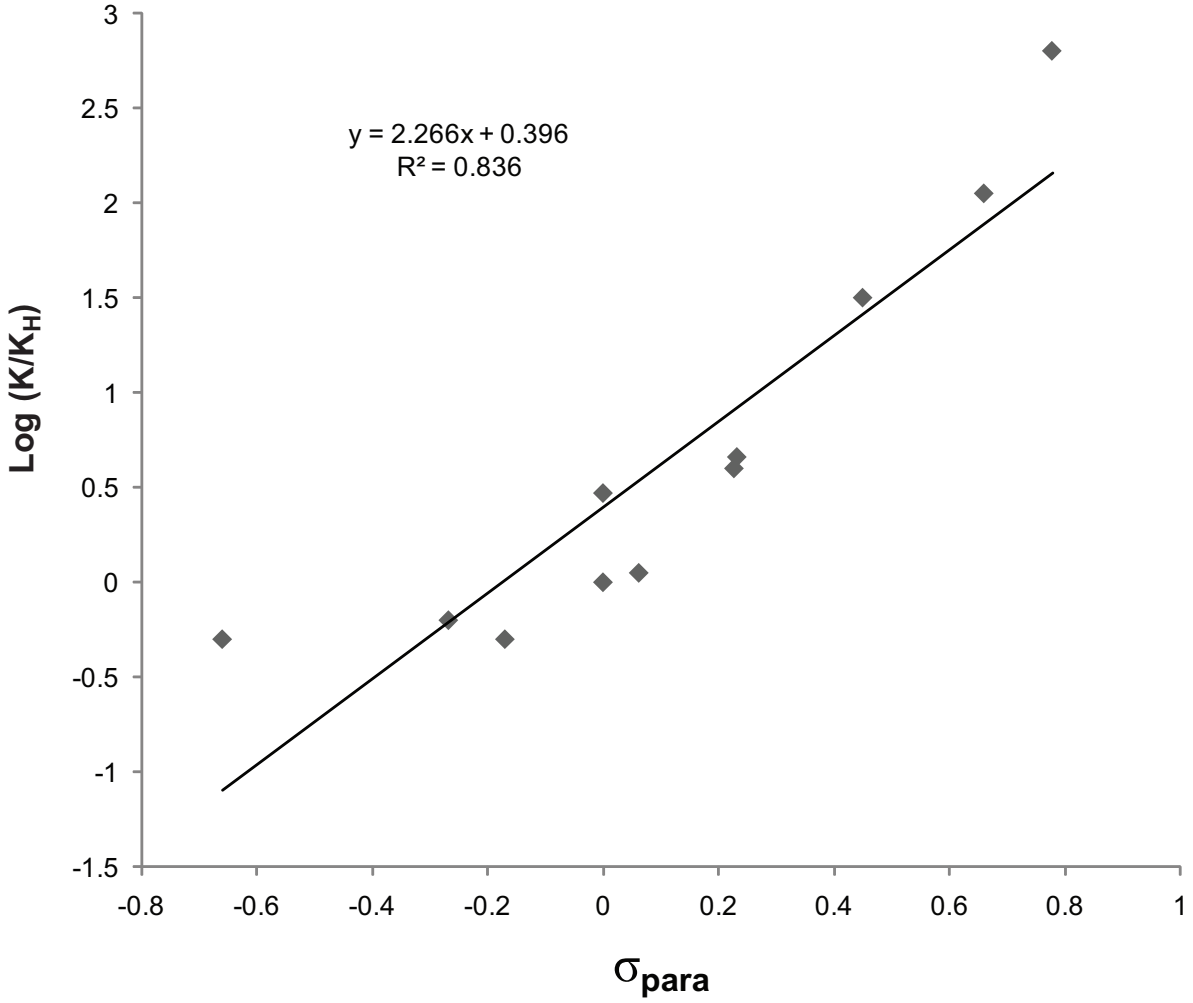
Activity 10B More Hammett Plots

Focus Question

How can Hammett Plots be used in determining a reaction's mechanism?

Model 1

Hammett Plot for the Dissociation of Phenol



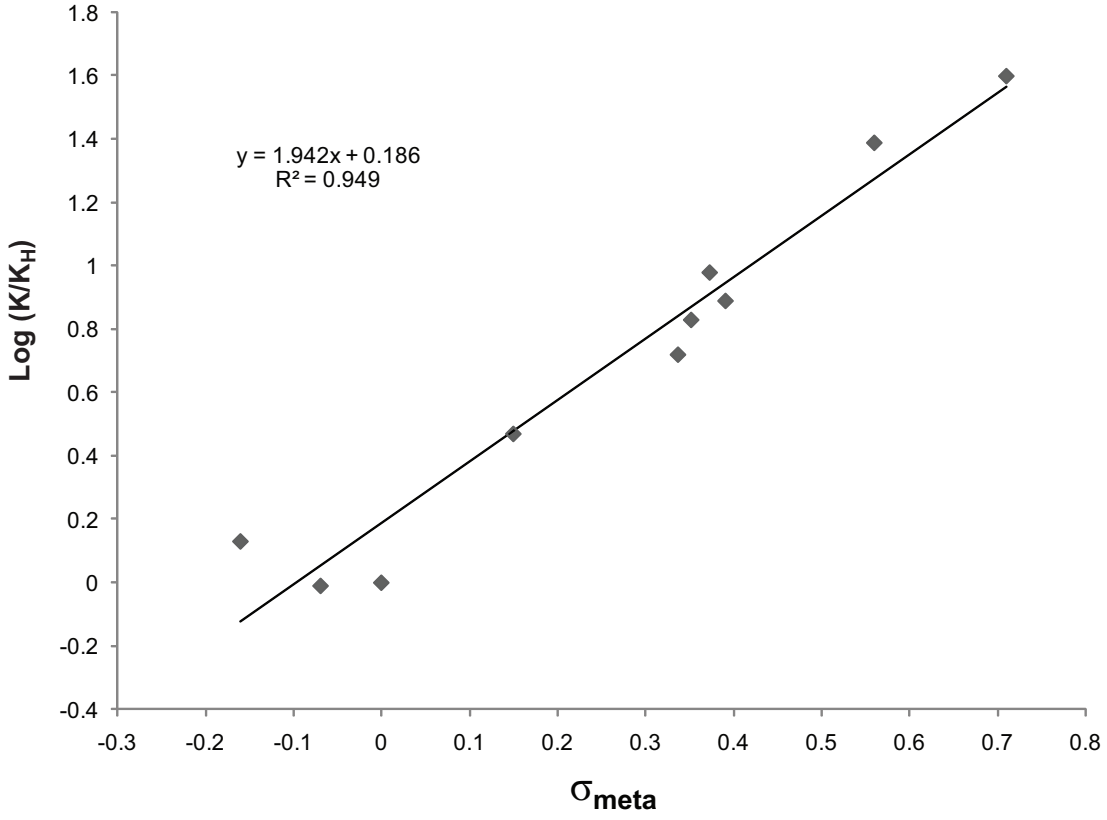
1. Is $\rho > 0$, $\rho < 0$, or does $\rho = 0$?

2. Draw out the dissociation of phenol into phenoxide and hydrogen ions.

3. Based on the reaction you drew, explain why ρ is positive.

4. What does the R^2 value indicate about the data plotted in Model 1?

5. Below is a Hammett plot of the dissociation of phenol, but this plot includes only substituents in the meta position. What does the R^2 value indicate about this graph compared to that in Model 1?



6. From the two plots in this model, compare the effects of para substituents on the dissociation of phenol versus the effects of meta substituent effects.

7. Why do you think that meta substituents affect the dissociation of phenol differently than do para substituents?

8. Draw out the conjugate bases of m-nitrophenol and m-nitrobenzoic acid and any important resonance structures.

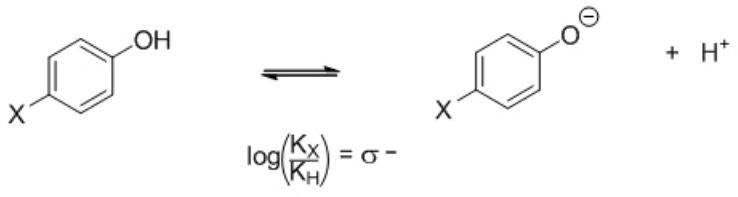
9. Do the same for the conjugate bases of p-nitrophenol and p-nitrobenzoic acid.

10. Do your answers to questions 8 and 9 support your answer to question 7? If so, explain how they do. If not, propose a different explanation.

Model 2

Resonance vs. Inductive effects

As you found out in the previous model, Hammett σ values do not take into account direct resonance stabilization of a negative charge. For these reactions, Hammett plots give curved lines, so a modified σ constant σ^- is used in these types of reactions. The σ^- scale is based on the dissociation of phenol.



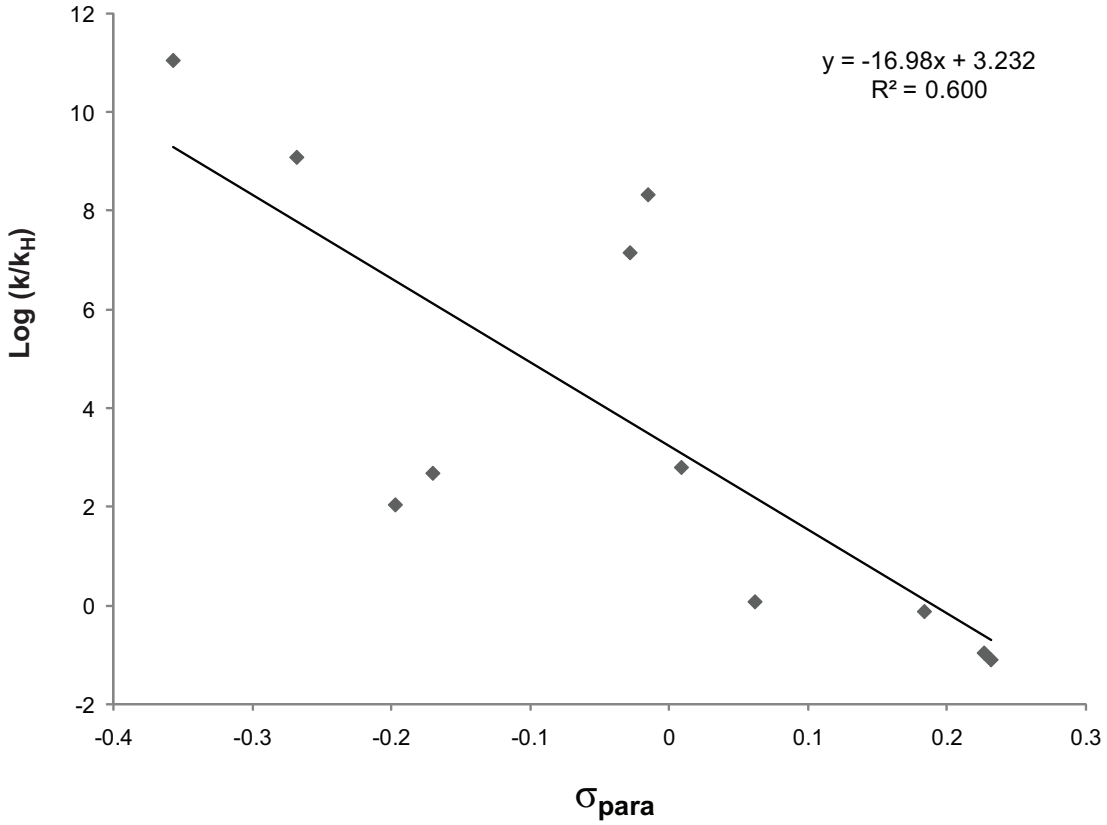
11. For what type of substituent is $\sigma^- > 0$?

12. For what type of substituent is $\sigma^- < 0$?

13. For what type of substituent is $\sigma^- = 0$?

Model 3

Hammett Plot of Electrophilic Aromatic Bromination



14. Draw out the mechanism of electrophilic bromination of benzene. Although this reaction is usually catalyzed by a Lewis acid, show the uncatalyzed version.

15. Circle the slowest step.

16. Why is log (k_X/k_H) used in this plot instead of log (K_X/K_H)?

17. What is the sign of ρ?

18. Use the mechanism of this reaction to explain why ρ is negative.

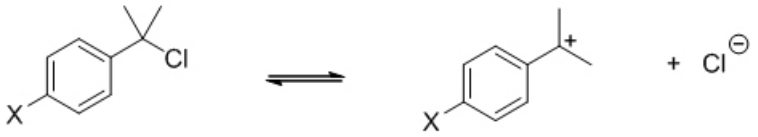
19. What does the R^2 value in Model 3 indicate about the Hammett plot of electrophilic aromatic bromination?

20. Propose an explanation for why the Hammett plot for electrophilic aromatic bromination with para substituents is not linear.

Model 4

t-Cumyl Chlorides

Because Hammett σ constants also do not take into account direct resonance stabilization of a positive charge, σ^+ constants are used in these cases. Their definition is based on the dissociation of *t*-cumyl chlorides.



$$\log\left(\frac{K_X}{K_H}\right) = \sigma^+$$

21. Draw curved arrow(s) to show electron flow in the above reaction.

22. For what type of substituent is $\sigma^+ > 0$?

23. For what type of substituent is $\sigma^+ < 0$?

24. For what type of substituent is $\sigma^+ = 0$?

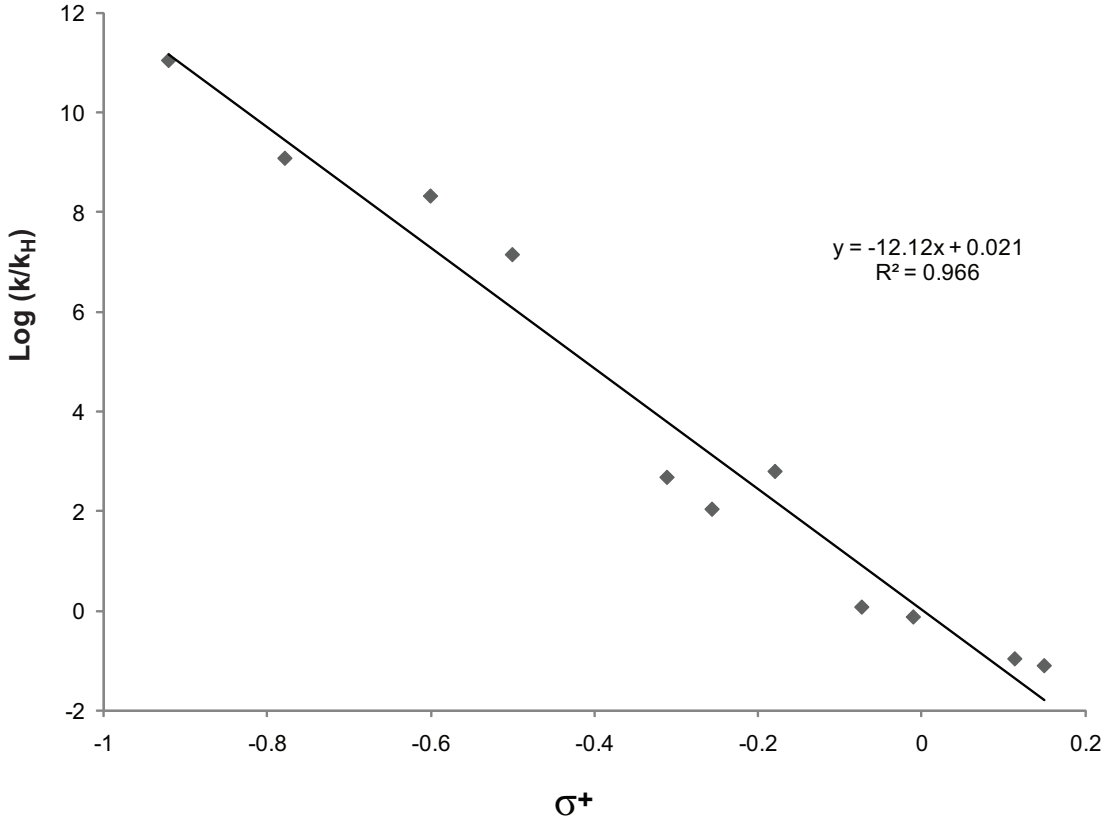
25. The σ^+ and σ^- values are defined so that electron withdrawing groups and electron donating groups have values that are the same sign as they do on the σ scale. Do your answers to questions 11-13 and 22-24 agree with this information?

26. Both the σ^+ and σ^- values for phenyl have been measured, and they have different signs ($\sigma^+ < 0$ and $\sigma^- > 0$). Explain this data.[1] Do not forget to draw resonance structures as part of your answer.

Model 5

Revisiting Electrophilic Aromatic Bromination

Below is a Hammett plot for electrophilic aromatic bromination using the σ^+ values.



27. What does the R^2 value indicate about the above Hammett plot?

28. From the plots in Model 3 and Model 5, what do you know about the rate determining step of this reaction?

29. Does your answer to 28 agree with your answer to 15?

1 Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry: Part A: Structure and Mechanisms*; Springer: New York, 2004; p. 251.