Funny Functional Groups with Dual Nature

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Abstract

It is a general leaning in a physical organic chemistry classroom both the teacher and the taught to be under the perception that the Hammett σ (log $\frac{K_X}{K_H}$ by definition setting Hammett ρ = 1 in water at 25°C) substituent constants of the substituents (X) are positive for electron withdrawing groups and negative for electron donating groups irrespective of the position of the substituent in the benzene ring and it is zero for hydrogen (H). But some functional groups like OH, O-alkyl and O-aryl behave differently with respect to their position in the benzene ring. These substituents behave like electron donors when they are in para position and electron acceptors when they are in Meta position. Explanations are presented in this piece of work for such behavior. And there is one lone strange functional group $(-CO_2^-)$ the carboxylate anion behaves like electron donor when it is in Meta position with a negative Hammett σ value and behaves like H when it is in para position with zero Hammett σ value yet doesn't follow pK_a trend.

Keywords: Hammett equation; σ substituent constants
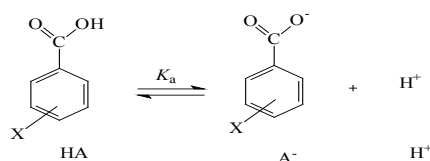
Introduction

The Hammett σ substituent constants were determined using dissociation constants (K_a) of the equilibrium (eqn. 1) of Meta and Para substituted benzoic acids and Hammett equation log (K_X/K_H) = ρσ setting a value of 1 for ρ in water at 25°C.[1]

$$K_a = XC_6H_4COOH \rightleftharpoons XC_6H_4COO^- + H^+ \qquad [1]$$

Methods

All the chemical structures are drawn using chemdraw. The pK_a values and Hammett substituents constants (σ) are from the references respectively [2-4].

First it is necessary to see that how the signs of substituent constants are attributed. The benzoic acid dissociation equilibrium is shown in **Scheme 1.**
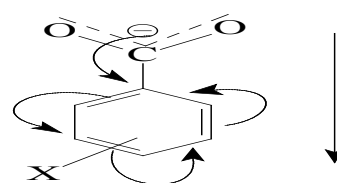

Scheme 1

There fore $K_a = \frac{[A^-][H^+]}{[HA]}$. K_a is the acid dissociation constant. Let it be represented as K_X for any substituted benzoic acid and K_H for benzoic acid itself. And the Hammett relation is as shown in equation 3:[1]

$$\log \frac{K_X}{K_H} = \rho\sigma \qquad [3]$$

Since ρ is given a value of 1 to estimate the σ value (ref), eqn. 3 becomes simply eqn. 4.

$$\log \frac{K_X}{K_H} = \sigma \qquad [4]$$

Here K_X and K_H are acid dissociation equilibrium constants of any substituted benzoic acid and benzoic acid itself respectively. If X is electron withdrawing the X substituted benzoate anion is more stable than the benzoate anion of the benzoic acid itself as the negative charge on the carboxyl group is pulled towards the substituent as shown in **Scheme 2.**

Scheme 2

Therefore more stable substituted benzoate anion with electron withdrawing substituent is less reactive than the benzoate anion to recombine with H^+ to go back to un-dissociated acid. Hence the equilibrium concentrations of substituted benzoate anion and H^+ are more than those of the benzoic acid resulting the product of [substituted benzoate anion] $[H^+]$ > [benzoate anion] $[H^+]$. Therefore K_H is > 1. As the logarithm of any number that is > 1 will be a positive value leads to a positive Hammett σ value. And the situation will be just reversed when X is electron donating group leads to give a negative Hammett σ values. Table gives the summary of Hammett σ values and the pK_a values of some benzoic acids **(Table 1)**.

It can be seen from the **Table 1**; the Hammett σ values of electron withdrawing substituents like CN and NO_2 are greater than the Hammett σ value of H (benzoic acid). And the benzoic acids with CN and NO_2 as substituents either in Meta or Para position are stronger acids than benzoic acid which is reflected from their lower pK_a values than 4.2 the pK_a value of benzoic acid. Similarly benzoic acids with electron donating substituents like NH_2 and N $(NH_2)_2$ as substituents either in Meta or Para position are weaker acids than benzoic acid which is reflected again from their higher pK_a values than 4.2. But some substituents like those shown in red in the table cannot be regarded as a general rule of thumb **(Table 1)**. When they are in para position they behave like electron donors and make the acid weaker than benzoic acid. This can be seen from their higher pK_a values than the value of 4.2 of benzoic acid. And it is expected that when they are in Meta position also they should behave as electron donors like the substituents NH_2 and N $(NH_2)_2$. But when they are in Meta position they behave like electron withdrawing and make the acid stronger than benzoic acid. This can be seen from their lower pK_a values than the value of 4.2 of benzoic acid.

Discussion

The possible explanations are: The substituents like O-alkyl and O-aryl groups posses lone pair of electrons on oxygen. If they are present in para position the lone pair of electrons participate in the resonance (mesomeric effect, - M effect) making benzoate anion unstable as shown in **Scheme 3.** This makes the acid weaker than benzoic acid with a higher pK_a value than 4.2 of benzoic acid.
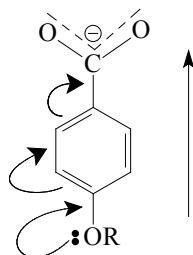

Table 1 Hammett σ constants and pKa values of X C_6H_4 COOH.

S. No.	X	σ_{Meta}	σ_{para}	pK_a Meta	pK_a para
1	H	0.00	0.00	4.20	4.20
2	CN	0.56	0.66	3.60	3.55
3	NO_2	0.71	0.80	3.47	3.41
4	NH_2	-0.16	-0.66	4.80	4.92
5	$N(CH_3)_2$	-0.20	-0.83	5.10	6.03
6	OCH_3	0.12	-0.27	3.84	4.37
7	OH	0.12	-0.37	4.08	4.58
8	$HNCOCH_3$	0.21	0.00	4.07	4.28
9	C_6H_5O	0.25	-0.32	3.95	4.52
10	OCH_2CH_3	0.10	-0.24	4.14	4.80
11	$OCH(CH_3)_2$	0.05	-0.45	4.15	4.68
12	CO_2^-	-0.10	0.00	4.46	4.82

Scheme 3

Writing such resonance structure like **Scheme 3** with the substituent O-alkyl or O-aryl group in Meta position is not possible. Therefore the electron density on the carboxyl group is less than in benzoate anion thus making the Meta substituted alkoxy/aryloxy benzoic acid more acidic with lesser pK_a values than 4.2 of benzoic acid and a fact that can be accounted for by the -I effect of these groups. In addition to that the oxygen in alkoxy/aryloxy is more electronegative than the π-carbons of the benzene ring.

A search for the substituents in Meta position with negative Hammett σ values and for the same substituents in para position with positive Hammett σ values is not that successful. I could find only one substituent $-CO_2^-$ with reported pK_{a2} values of both isophthalic acid and terphthalic acid anions **(Table 1**, in deep blue) out of 530 Hammett substituents constants reported. This is the one benzoic acid with $-CO_2^-$ as substituent in Meta and Para position is found with this trend of Hammett σ substituent constants whose pK_a values are known. Even this acid did not follow the general rule of thumb. As expected with $-CO_2^-$ as substituent in Meta position with negative σ value of -0.10 had a higher pK_a than 4.2 of that benzoic acid. But with $-CO_2^-$ as substituent in para position with positive (here it is 0.00 which is more positive than -0.10) σ value should have a lesser pK_a than 4.2 of that benzoic acid or at least it should have a pK_a value of 4.2 equal to that of benzoic acid as the σ_{para} of $-CO_2^-$ is zero. But its pK_a value is 4.82 is higher than 4.2 of benzoic acid which could not be explained at the moment.

Conclusion

As a conclusion the title of this piece of work warrants that the substituents from 6-12 look strange to see their Hammett σ values and they had a dual nature.

References

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