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The attenuation effect through methylene group*

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There are several hundreds of redox, condensation, disproportionation, nucleophilic and electrophilic substitution, and addition reactions with *meta*- and *para*-substituted benzene derivatives in the literature, for which the Hammett reaction constants (ρ) were reported. If benzene can deprotonate behaving like a carboxylic acid, what could be the Hammett ρ value for such kind of equilibrium reaction?

$$(XC_6H_5 \overset{K_a}{\rightleftharpoons} XC_6H_4^- + H^+)$$

Here the author has tried to evaluate such Hammett ρ value by a simple and new protocol using of attenuation effect of a methylene group on benzoic acid dissociation equilibriums.

Key words: Attenuation effect, methylene group, acid dissociation equilibriums.

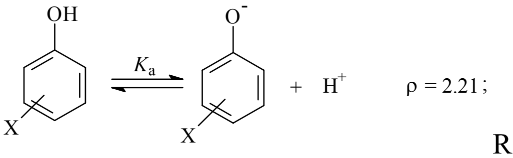
The effect of structure on the benzoic acid dissociative equilibria (K_a) and subsequently on chemical reactivity (k) is well explained by the putative Hammett equation (1). Based on the concept of this equation several hundreds of papers have emerged in chemical literature in the last century on the effect of structure on reactivity. It relates acid dissociative equilibria (K_a) or the chemical reactivity (k) in *meta*- and *para*-substituted benzene derivatives in terms of two parameters, the reaction constant (ρ) and the substituent constant (σ). Thus the equation proposed by Hammett for acid dissociative equilibria (K_a) is

$$\log K_a^X = \log K_a^H + \rho\sigma \qquad (1)$$

where K_a^X is the dissociation constant of substituted benzoic acid and K_a^H is that for the unsubstituted benzoic acid in water at 25°C, ρ is the reaction constant and σ is the substituent constant and for chemical reactivity (k), it is:

$$\log k_X = \log k_H + \rho\sigma \qquad (2)$$

where k_X is the rate constant for the substituted benzene derivative and k_H is for unsubstituted benzene derivative. Using equation 1 and a value of unity is chosen arbitrarily for ρ in aqueous solution and at 25°C, the σ values were evaluated. Using such σ values equation 2 is applied to several reactions to explain the effect of structure on reactivity. The value of ρ is a measure of the magnitude of the effect of structure either on acid dissociation equlibria or on the reactivity of *meta*- and *para*-substituted benzene derivatives. First, let us consider the acid dissociation equilibria of different oxygen containing acids in aqueous solution with increasing length of carbon chain between the ionizable proton and the aromatic ring carbon.



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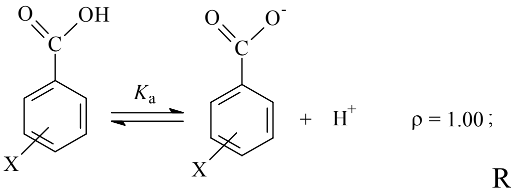

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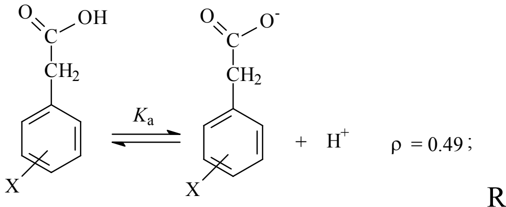

Ref. 2 (5)

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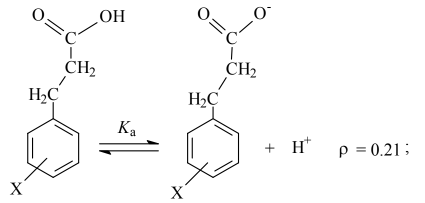

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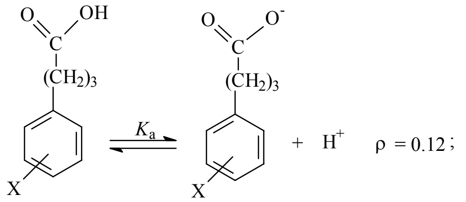


Ref. 3 (7)

The substituent effects can be transmitted in three ways: (i) inductive effects, (ii) steric effects and (iii) resonance effects. The first two kinds of effects naturally diminish very rapidly as the distance between the reaction center and the substituent increases. The third one is very effective due to polarization of the π-electron system conjugated by resonance and it is due to mutual intervening conjugation between substituent and the reaction center. And also the substituent effect through the resonance due to polarization of the conjugated π-electron system will be strongly affected and will decrease rapidly upon introducing an increasing number of methylene groups between the ionizable proton and the ring carbon atom in the dissociation of benzoic acid series. This could be observed in the above acid dissociation equilibriums. The ρ value decreases as the number of methylene groups increases. This effect was explained by Andrew Williams (4) by proposing an empirical equation (Eqn. (8)) and back calculating the Hammett ρ values for the dissociation equilibriums of phenols and phenyl acetic acids, which were found to be close to those determined experimentally.

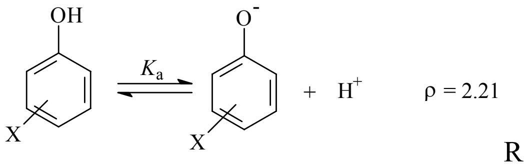
$$\rho = (2.4)^{2-i} \qquad (8)$$

where 'i' is the number of atoms between the ionizable proton and the ring carbon atom of benzoic acids. This could be seen as a beautiful exponential decay curve as it is shown in the figure by extending the application of Eqn. (8) further to dissociation equilibriums of benzoic, and other two acid series. From the figure one can always expect the ρ value to be a function of the number of methylene carbons or *vice versa*. But the reduction in the ρ value is by more than 50% comparing phenol dissociation to benzoic acid dissociation. Whereas going from benzoic acid dissociation onwards it is a systematic reduction in the ρ value each time by 50% only. This could be due to introduction of a sp^2 hybridized carbon atom (>C=O), which can probably provide an additional stabilization to the carboxylate anion of the benzoic acid. And from benzoic acid onwards the carbon chain is increased each time with one sp^3 hybridized carbon atom.

Further the large difference in substituent effects between the benzoic acid and the phenol series is well explained by Wiberg (5). It can result from strong field effect due to the decreased distance between the negative charge and the substituents in the phenoxide ions, compared to benzoates. The increased negative charge in the ring of the phenoxides results from π-donation from the anionic site and it enables a direct π-electron interaction between the phenoxide ion and the substituents. This type of interaction is not present in the benzoate ions.

In the study of substituent effects on benzoic acids, a particularly useful comparison was made between benzoic acids and the corresponding phenylacetic acids. Here, a very good linear relationship was found. Since the CH_2 group acts like an insulator, which prevents a direct π-electron interaction. The linear relationship showed that in both series the substituents effects have a common origin and they result from a Coulombic field effect of interaction of the carboxylate group with the charge distribution in the aromatic ring that was caused by the substituents.

Another striking and interesting comparison is between the dissociation equilibria of phenols and the corresponding benzyl alcohols.



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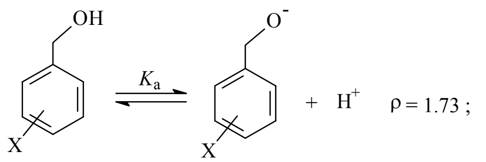
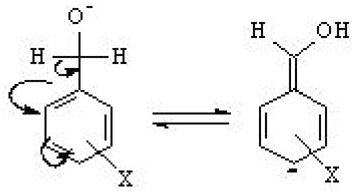


Ref. 6 (9)

One might be concerned about the ability of the CH_2 group in benzyloxide anion to act as a π-insulator (Eqn. 9). Here the Hammett ρ value for benzyl alcohols dissociation equilibria should be simply 1.11, which is half of that of phenoxide ion equilibria, based on the fact that the Hammett ρ value for phenyl acetic acids has become reduced to half of that of benzoic acids again upon the introduction of one CH_2 group between the carboxylate carbon and the benzene ring carbon. But the actual ρ value was found to be 1.73 (6). One putative explanation of this, offered by Wiberg (5), is: In gas-phase alkoxide ions, the negatively charged oxygen atom polarizes the C–H bonds, placing considerable negative charge at the hydrogen atoms and a positive charge at the carbon atom. The carbon has an attractive Coulombic interaction with the negatively charged oxygen, leading to a shorter C–O bond, which may lead to somewhat larger substituent effect and in turn in aqueous solution even larger. Another explanation may come from the hyperconjugation of the benzyloxide ion, which may be even further stabilized by charge delocalization onto benzene ring as it is shown below (Eqn. (10)) to contribute towards higher Hammett ρ value.

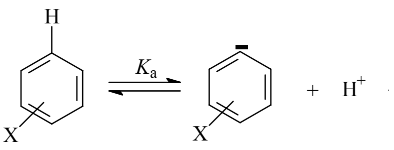


(10)

And this kind of effect is not present in benzoic acid, where the entire negative charge is concentrated on carboxylate group.

In conclusion, the introduction of an sp^2 hybridized carbon (>C=O) reduces the ρ value by a factor of more than 50% (2.21 to 1.00), when we go from phenol dissociation to benzoic acid dissociation, where the introduction of an sp^3 carbon ($–CH_2–$) reduces the ρ value by a factor of only 22% (2.21 to 1.73), which could be interpreted to the effect that the $–CH_2–$ is a good π-interaction insulator.

From Eqn. (8), it is clear that if $i = 0$ i.e. if there are no atoms between the ionizable proton and the benzene ring carbon, the example would be benzene itself, the Hammett ρ value would be 5.76 ($\rho = 2.4^{(2-i)} = 2.4^{(2-0)} = (2.4)^2$) for such system, if anybody determined it (see below the dissociation equilibrium, Eqn. (11)). It can also be seen from the graph by interpolation, the Hammett ρ value turns out to be 5.42, which is close to 5.76. But to the author's knowledge, nobody has determined the Hammett ρ value for such dissociation equilibrium. Also it could be further concluded that the Hammett ρ value should not exceed 5.76 for any kind of reactions, involving *meta*- and *para*-substituted benzene derivatives.



(11)

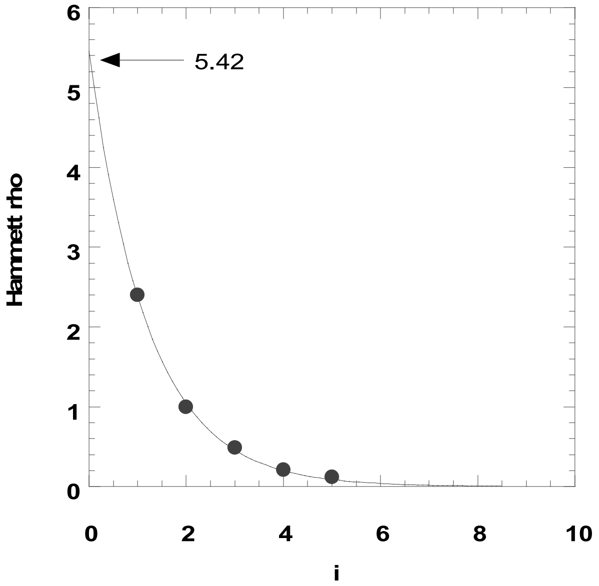


Fig. 1. Plot of Hammett ρ versus the number of atoms between the ionizable proton and ring carbon.

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6. The ρ value for this equilibrium is an estimate based on the correlation of gas-phase ΔH_{acid} values (5) of different oxygen containing acids and is done as follows: The Hammett ρ value for phenol dissociation equilibriums in aqueous solution is 2.21 (2). The gas-phase ρ value for this same equilibrium is 1.28 (5). Hence the ratio (ρ_{aq}/ρ_{gas}) is 1.73. The Hammett ρ value from the correlation of gas-phase ΔH_{acid} values of benzyl alcohols versus those of phenyl acetic acids is 1.00 (5). Therefore the Hammett ρ value for benzyl alcohols dissociation equilibria in aqueous solution on benzoic acid dissociation scale would be: (ρ of phenyl acetic acids) x (ρ_{aq}/ρ_{gas}) = 1.00 x 1.73 = 1.73.

ЕФЕКТ НА СПРЯГАНЕ ПРЕЗ МЕТИЛЕНОВА ГРУПА

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(Резюме)

В литературата има няколкостотин редокс реакции, реакции на кондензация, диспропорциониране, нуклеофилно и електрофилно заместване, на присъединяване с *мета*- и *пара*-заместени бензенови производни, за които са дадени константите на реакцията на Хамет (ρ). Ако бензен може да се депротонира, действайки като карбоксилова киселина, каква трябва да бъде стойността на ρ за тази равновесна реакция:

$$(XC_6H_5 \overset{K_a}{\rightleftharpoons} XC_6H_4^- + H^+)$$

Авторът се е опитал да оцени стойността на константата на реакцията на Хамет чрез нова и лесна за изпълнение процедура, използвайки ефекта на метиленовата група върху дисоциационните равновесия на бензоените киселини.