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# Attenuation effect through methylene group: Part II [1]

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A simple, new and lucid protocol is presented in this article for the evaluation of the Hammett reaction constant (ρ) of the deprotonation process of arenium ions $XC_6H_6^+ \rightleftharpoons XC_6H_5 + H^+$ based on the attenuation effect of methylene group on the dissociation equilibriums of anilinium ions, benzyl ammonium ions and 2-phenylethyl ammonium ions.

**Key words:** Hammett reaction constant (ρ), attenuation effect, arenium ions.

## INTRODUCTION

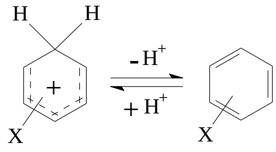
Benzoic acid dissociation equilibriums and the chemical reactivity of *meta*- and *para*-substituted benzene derivatives were well explained by Hammett equation[2] in terms of two parameters the Hammett substituent constant (σ) and the Hammett reaction constant (ρ). Thus the Hammett equation for benzoic acid dissociation equilibriums is:

$$\mathbf{\log K_X = \log K_H + \rho\sigma} \qquad \mathbf{(1)}$$

$K_X$ and $K_H$ are acid dissociation constants of substituted and un-substituted benzoic acids respectively. The Hammett reaction constant (ρ) is a measure of the magnitude of the effect of structure on the benzoic acid dissociation equilibriums.

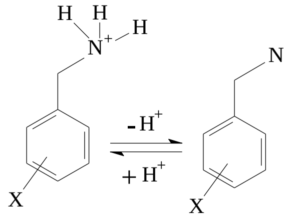
## DISCUSSION

First let us see the dissociation equilibriums of arenium ions and different aryl ammonium ions with increasing length of carbon chain between ionizable proton and the ring carbon atom.



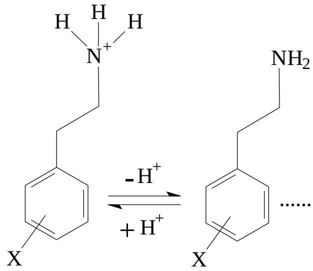
........(2) Hammett's ρ = 17.1

number of atoms between ionizable proton and ring carbon atom = 0



............(4) Hammett's ρ = 1.06

number of atoms between ionizable proton and ring carbon atom = 2



..............(5) Hammett's ρ = 0.61

number of atoms between ionizable proton and ring carbon atom = 3

To the best of the authors knowledge, as the p$K_a$ values were not available of the arenium ion dissociations in literature, the Hammett reaction constant (ρ) for the equilibrium 2 i.e. for the dissociation of arenium ions was evaluated from the relative stabilities[3] as a function of Hammett σ values. The Hammett reaction constant (ρ) for the equilibriums 3 and 4 were evaluated from the respective plots of p$K_a$ values of the dissociation equilibriums of anilinium and benzyl ammonium ions versus Hammett σ values. The p$K_a$ values of dissociation equilibriums of anilinium ions and benzyl ammonium ions are from references 4 and 5 respectively. The Hammett reaction constant (ρ) for the equilibrium 5 was evaluated from the p$K_a$ values of only two 2-phenylethyl ammonium ions[6], one is un-substituted and the other is 4-OH substituted.

The substituent effects from the benzene moiety could be spread effectively to the reaction center through resonance. The spreading is more predominant if the conjugated π-electron system is present between the reaction center and the substituent and due to its polarization. This will diminish more rapidly upon introducing methylene groups between the ionizable proton and the ring carbon atom. The $sp^3$ hybridized –$CH_2$– group acts as a σ-electron insulator.

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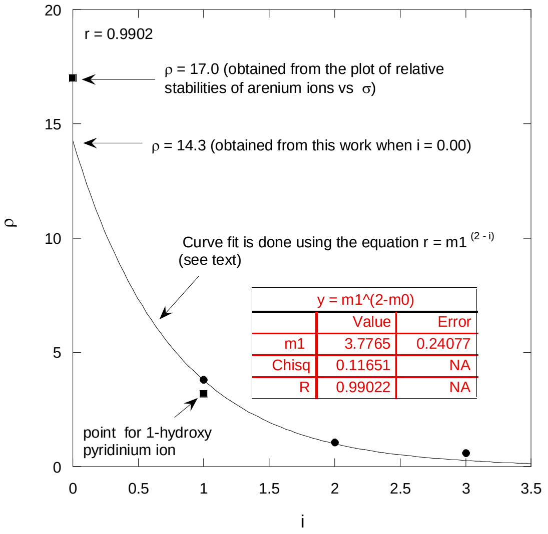
This is observed in the above equilibriums 2-5. As such the Hammett reaction constant ($\rho$) decreases as the number of methylene groups are increased. This is well explained by Andrew Williams[7] by an empirical equation (eqn. 6):

$$\boldsymbol{\rho = m_1^{(2-i)}} \qquad \textbf{(6)}$$

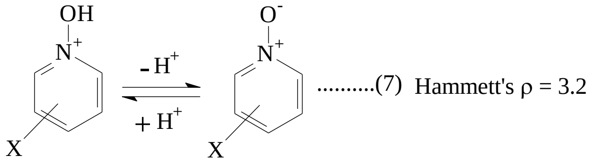
Where '$m_1$' is a constant and 'i' is the number of atoms between the ionizable proton and the ring carbon atom. This could be seen as a beautiful exponential decay curve (figure 1):

Figure 1: Plot of Hammett ρ versus i ( the number of atoms between the ionizable proton and the ring carbon)



From equation 6 it is clear that if i = 0, i.e. if there are no atoms between the ionizable proton and the ring carbon atom, the example would be arenium ion itself. Then the Hammett $\rho$ value would be $m1^{(2-i)} = m1^{(2-0)}$. Here, from the curve fit of the data, m1 was found to be 3.78 (see box in the figure). Thus the Hammett $\rho$ value would be $(3.78)^2 = 14.3$. The value obatained from the Hammett plot of arenium ion stabilities versus Hammett $\sigma$ was found to be 17.0. The value from the present work is less by a factor of 1.19 than the calculated value from arenium ion stabilities. Yet the trend is unmistakable.

Another notable observation is that about the Hammet $\rho$ value for the dissociation equilibriums of 1-hydroxy pyridinium ions (equilibrium 7). 1-hydroxy pyridinium ion is nothing but the protonated pyridine-N-oxide.

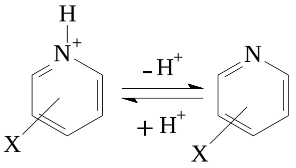


..........(7) Hammett's $\rho = 3.2$

number of atoms between the ionizable proton and the ring atom is zero

Hammet $\rho$ value of 3.2 of this dissociation equilibrium is obatained from the plot of $pK_a$ versus Hammett $\sigma$ values. The $pK_a$ values are from reference 8. The Hammtt $\rho$ value, though it did not fall on the line of fit of the plot of $\rho$ versus i but it is very close to the line of fit (figure 1). This clearly shows that whether the benzene ring atom is carbon or nitrogen and whether it is a nitrogen acid or oxygen acid, if the number of atoms between the ionizable proton and the ring atom are same for two types of acid dissociation equilibriums, the Hammett $\rho$ values would be more or less the same. Here it is the comparision between the dissociation equilibriums of 1-hydroxy pyridinium ions and anilinium ions for which there is only one atom between ionizable proton and the ring atom. In the case of 1-hydroxy pyridinium ion it is 'oxygen' and in the case of anilinium ion it is 'nitrogen'. Therefore it is not the nature of a particular atom that plays the role but it the only number that matters in creating the $\sigma$-electron insulation. But the atom should have an $sp^3$ hybridization.

The following equilibrium (equation 8) is the dissociation of pyridinium ions. The value of 'i' is zero. That is there are no atoms between inizable proton and the ring atom.



..........(8) Hammett's $\rho = 6.6$

number of atoms between the ionizable proton and the ring atom is zero

Hence it should reflect the property of the dissociation of arenium ions with respect to Hammett $\rho$. But to our surprise the Hammett $\rho$ value obtained from the plot of $pK_a$ versus Hammett $\sigma$ value was found to be only 6.65 which is far less than the value of 14.3 obtained form this work or 17.1 from the arenium ion stabilities. The $pK_a$ values of pyridinium ion dissociation equilibriums are from references 8 and 9. This discrepancy could not explained at present.

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# ЕФЕКТ НА ОСЛАБВАНЕ НА МЕТИЛЕНОВИ ГРУПИ: ЧАСТ II

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(Резюме)

В тази статия се представя нов прост и ясен протокол за изчисляване на реакционната константа на Хамет (ρ) за процеса на депротониране на арениеви йони , базиран ослабване на метиленови групи според дисоциационните равновесия на анилинови йони, бензил-амониеви йони и 2-фенилетил амониеви йони.