



Journal of Applicable Chemistry

2014, 3 (2): 440-448

(International Peer Reviewed Journal)



Effect Of Hybridization Of Carbon On Hammett Reaction Constant (ρ): π -Electron Transmission Versus σ -Electron Insulation: A Motivating Lecture For Graduate Students Of Physical-Organic Chemistry Class-Room

V. Jagannadham^{1*} and R. Sanjeev²

1. Department of Chemistry, Osmania University, Hyderabad-500007, **INDIA**

2. Department of Chemistry, Avanathi Degree and PG College, Hyderabad-500029, **INDIA**

Email: jagannadham1950@yahoo.com

Accepted on 2nd February 2014

ABSTRACT

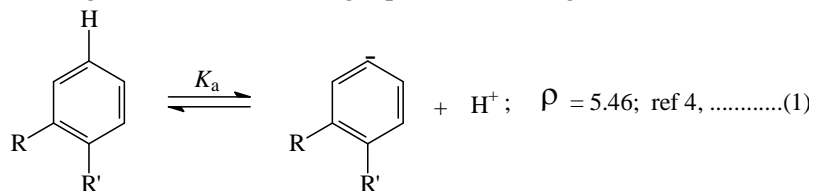
The presence of sp^2 carbons in a side chain of benzene ring resulted in a significant increase in Hammett ρ value by a factor of two in the dissociation equilibria of cinnamic acids ($XC_6H_4CH=CHCOOH$) and by a factor of five in the dissociation equilibria of 5-phenylpenta-2,4-dienoic acids (cinnamylidene acetic acids; $XC_6H_4CH=CH-CH=CHCOOH$) compared to the dissociation equilibria of phenyl propionic acids ($XC_6H_4CH_2CH_2COOH$) and 5-phenylpentanoic acids ($XC_6H_4CH_2CH_2CH_2CH_2COOH$) respectively. This concept is explained in a simple protocol based on the fact that σ bonds are localized. They form the covalent bonds between the carbon atoms. The π electrons in a conjugated double bond system are not relatively localized and not as strongly bound as the σ electrons. Only π -electron transmission through sp^2 carbons in cinnamic acids and 5-phenylpenta-2,4-dienoic acids is solely responsible for high values of Hammett ρ . And σ -electron insulation coupled with attenuation effect of two and four methylene groups in phenyl propionic acid and 5-phenylpentanoic acid dissociation equilibria respectively ended with very low Hammett ρ values. This is undoubtedly an interesting lecture for graduate students of physical-organic chemistry class-room. The presence of sp carbons in the side chain has affected the Hammett's ρ value in the 5-phenylprop-2,4-dienoic acid ($XC_6H_4C\equiv C-C\equiv C-COOH$) equilibria even more effectively when compared to the dissociation equilibria of 5-phenylpentanoic acids ($XC_6H_4CH_2CH_2CH_2CH_2COOH$) again.

Keywords: Attenuation effect, methylene group, acid dissociation equilibria, π -electron transmission, σ -electron insulation.

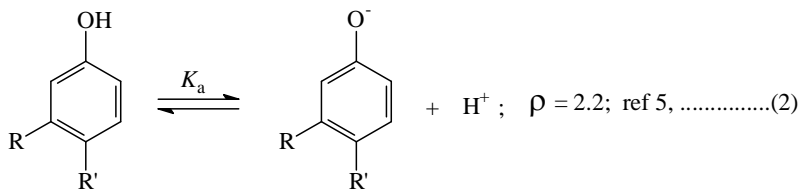
INTRODUCTION

The effect of structure on dissociation equilibria of *meta* and *para* substituted benzoic acids and reactivity of *meta* and *para* substituted benzene derivatives is a well documented phenomenon in physical-organic chemistry based on Hammett equation [1,2,3], $\log K_a^X = \log K_a^H + \rho\sigma$ or $\log k_X = \log k_H + \rho\sigma$. K and k have their usual significance. σ is the Hammett substituent constant. The value of Hammett ρ is a measure of the magnitude of the effect of substituent at *meta* and *para* position of substituted benzoic acids on the dissociation equilibria or reactivity of the respective *meta* and *para* substituted benzene

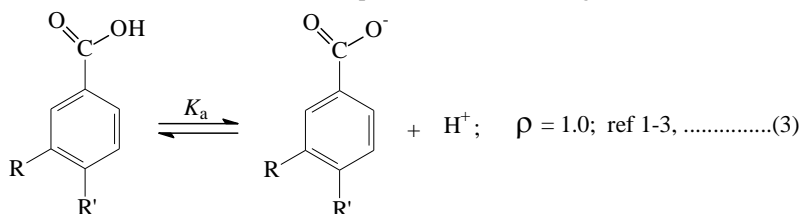
derivatives. Recollecting the acid dissociation equilibriums of different oxygen acids (except benzene which is a carbon acid) in aqueous solution with increasing length of carbon chain between the ionizable proton and the benzene ring carbon, the following equilibriums are given:



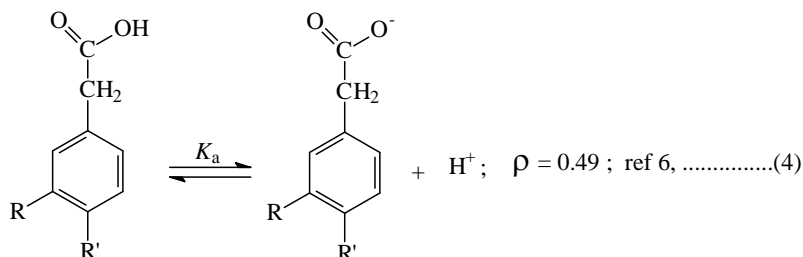
number of atoms between ionizable proton and benzene ring carbon atom is **zero**



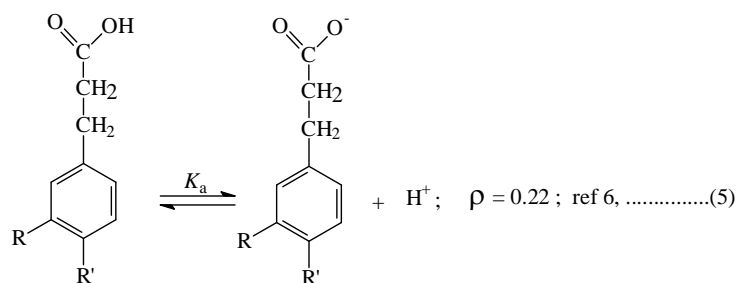
number of atoms between ionizable proton and benzene ring carbon atom is **one**



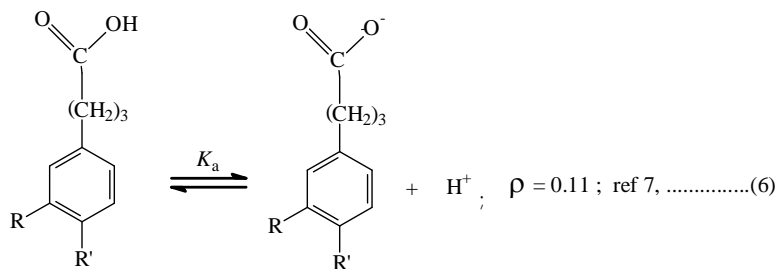
number of atoms between ionizable proton and benzene ring carbon atom is **two**



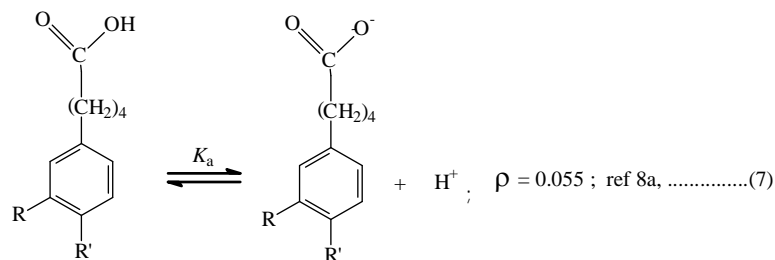
number of atoms between ionizable proton and benzene ring carbon atom is **three**



number of atoms between ionizable proton and benzene ring carbon atom is **four**



number of atoms between ionizable proton and benzene ring carbon atom is five



number of atoms between ionizable proton and benzene ring carbon atom is six.

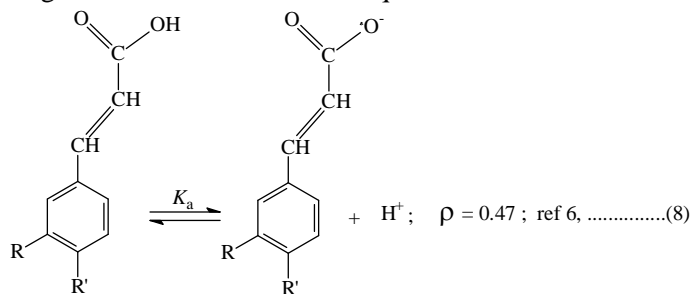
In the other two acids $\text{XC}_6\text{H}_4(\text{CH}_2)_n\text{COOH} \rightleftharpoons \text{XC}_6\text{H}_4(\text{CH}_2)_n\text{COO}^- + \text{H}^+$ with $n = 5$ and $n = 6$, the Hammett ρ values were found to be zero from their $\text{p}K_a$ values [8b].

From the above nine equilibria it is clear that the magnitude of the Hammett ρ decreases (approaching zero when the number of atoms are six between ionizable proton and the benzene ring carbon) each time by a factor of close to two with increasing distance step wise by a single atom between the reaction site and the benzene ring carbon and in turn the substituent. The data was nicely fit in to the exponential equation

$$\rho = (2.35)^{(2-x)}$$

proposed by Andrew Williams [9] (fig. 1), where 'x' is the number of atoms between the ionizable proton and the benzene ring carbon atom and the points for cinnamic acid and 5-phenylpenta-2,4-dieoic acid are shown separately. This substantial and gradual decrease of Hammett ρ was explained as follows: The substituent effects can usually be transmitted in three ways: (i) inductive effects, (ii) steric effects and (iii) resonance effects. The first two effects naturally diminish very rapidly in the above equilibria with increase in distance between reaction site and the substituent. The third one is absent except in the equilibria 1 and 2.

But an acid like cinnamic acid with four atoms between the ionizable proton and the benzene ring carbon and with two sp^2 hybridized carbons in the side chain is supposed to have a Hammett ρ of 0.22 at first sight similar to that of phenyl propionic acid in which the number of atoms between the ionizable proton and the benzene ring carbon is again four. The dissociation equilibrium of cinnamic acid is shown below:

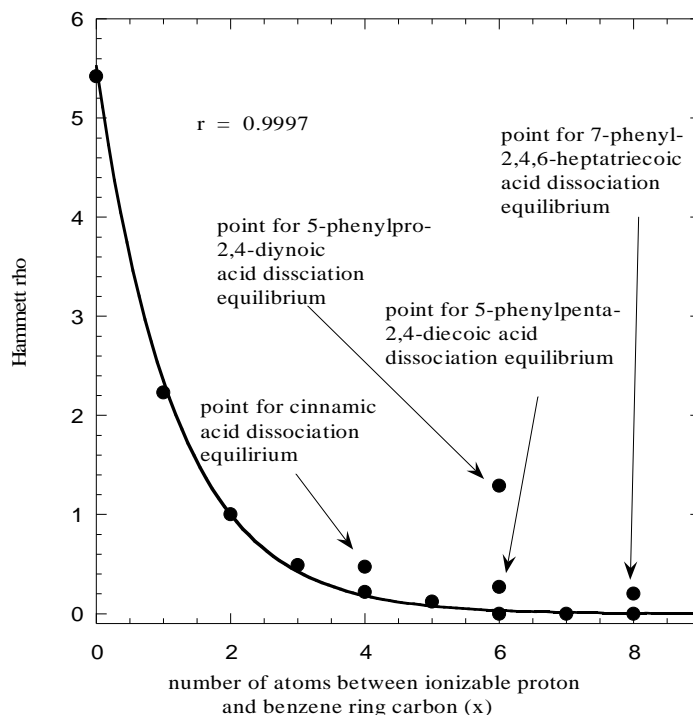


number of atoms between ionizable proton and benzene ring carbon atom are four

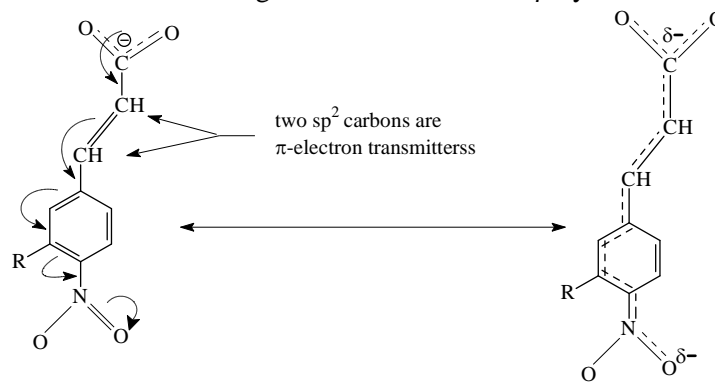
But the experimentally observed Hammett ρ for this equilibrium is 0.47, which is greater by a factor of two than that of the value for phenyl propionic acid [6] though they have same number of atoms between the ionizable proton and the benzene ring carbon atom (fig. 1). The third electronic effect mentioned above

is effective in cinnamic acid due to polarization of the π -electron system conjugated by resonance and it is due to mutual intervening conjugation through π -electron transmission between substituent and the reaction center as shown below taking nitro group as a typical substituent at *para* position. σ bonds are localized and form covalent bonds between the carbon atoms.

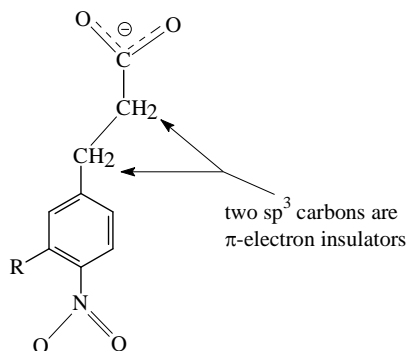
Fig 1: Plot of Hammett rho versus number of atoms between ionizable proton and benzene ring carbon



While the π electrons in a conjugated double bond system are not relatively localized and not as strongly bound as the σ electrons but effectively delocalized and can move along the molecular chain. Eventually some fraction of the negative charge is relieved from the carboxylate group and transmitted to the nitro group as shown below. Or the negative charge on the carboxylate group and the positive charge on the adjacent sp^2 carbon constitute a successful dipole making the carboxylate anion little more stable. Hence it is understood that the two sp^2 carbons are responsible for the stabilization of the carboxylate anion of the cinnamic acid which is reflected from the higher value of Hammett ρ by a factor of two.

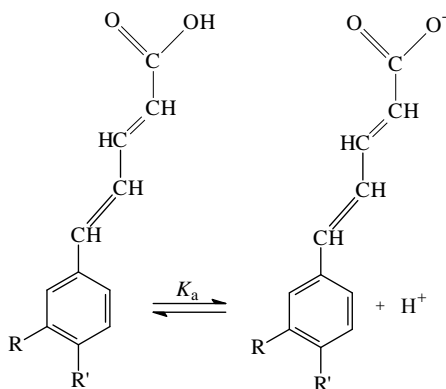


While in the case of phenyl propionic acid, the lower value of Hammett ρ (equation 5) is explained in terms of weak σ -electron interaction. The two sp^3 carbons act like electron insulators with the absence of π -electron interaction resulting in the localization of the total unit negative charge of carboxylate anion on carboxylate group itself, which makes the phenyl propionate anion less stable compared to that of cinnamic acid carboxylate anion as shown below:

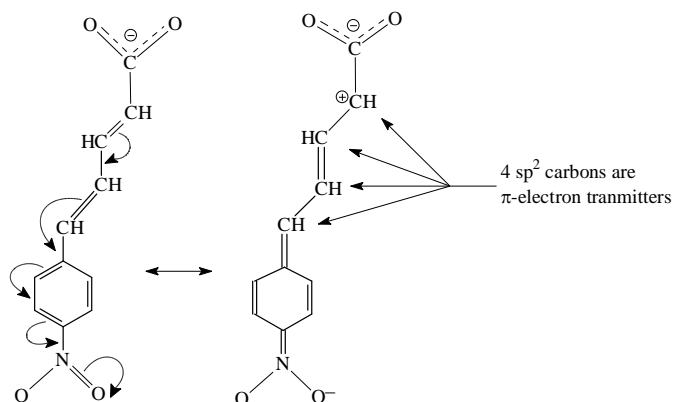


Hence a smaller Hammett ρ value of 0.22 [6] was observed for the equilibrium 5.

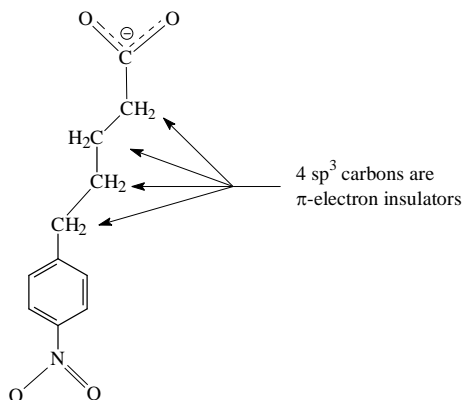
Similarly an acid like 5-phenylpenta-2,4-dienoic acid with six atoms between the ionizable proton and the benzene ring carbon and with four sp^2 hybridized carbons in the side chain is supposed to have a Hammett ρ of 0.055 [8] similar to that of 5-phenyl pentanoic acid in which the number of atoms between the ionizable proton and the benzene ring carbon is again six. The dissociation equilibrium of 5-phenylpenta-2,4-dienoic acid is shown below:



But the experimentally observed Hammett ρ for this equilibrium is 0.27 [10], which is greater by a factor of five than that of the value for 5-phenylpentanoic acid[8] though they have same number of atoms between the ionizable proton and the benzene ring carbon atom. As earlier it is understood that the four sp^2 carbons are highly effective which can provide an additional stabilization to the carboxylate anion of the 5-phenylpenta-2,4-dienoic acid with a higher value of Hammett ρ by a factor of five. The effect of four sp^2 carbons in 5-phenylpenta-2,4-dienoic acid is thus found to be more significant here as shown below considering nitro group as substituent in the *para* position:

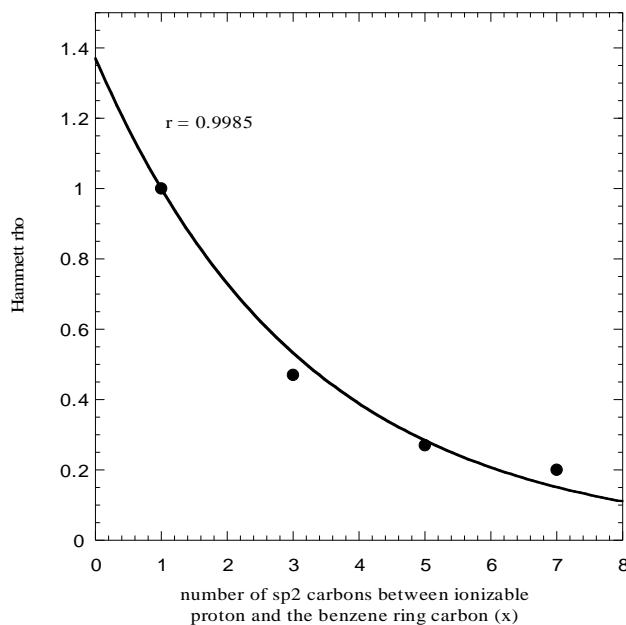


Again invoking the same argument given on page 4, for the case of 5-phenylpentanoic acid, the lower value of Hammett ρ (equation 7) is explained in terms of the no or weak σ -electron interaction. The four sp^3 carbons act like electron insulators again with the absence of π -electron interaction resulting in the localization of the total unit negative charge of carboxylate anion on carboxylate group itself makes the 5-phenylpentanoic acid carboxylate anion less stable compared to that of 5-phenylpenta-2,4-dienoic acid carboxylate anion as shown below:



From the four dissociation equilibria of benzoic acid, cinnamic acid, 5-phenylpenta-2,4-dienoic acid and 7-phenylhepta-2,4,6-trienoic acid it is clear that the magnitude of the Hammett ρ decreases each time by a factor of close to two with increasing distance step wise by a pair of sp^2 carbons between the reaction site and the benzene ring carbon and in turn the substituent. Considering the above rho values for different equilibria an exponential relationship has been obtained with the number of sp^2 carbon atoms (x) present between the ionizable proton and the benzene ring carbon akin to the relationship proposed by Williams [9] (Fig. 2).

Fig. 2: Plot of Hammett rho versus number of sp² carbons between ionizable proton and the benzene ring carbon



$$\rho = (1.37)^{(1-x)}$$

The only weakness with this equation is that it cannot be applicable to phenol dissociation equilibrium ($\rho = 2.2$) where there are no sp² carbons between the ionizable proton and the benzene ring carbon.

The presence of sp carbons in the side chain has affected the Hammett's ρ value (1.29) in the 5-phenylprop-2,4-diyneic acid ($\text{XC}_6\text{H}_4\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{COOH}$) dissociation equilibria even more effectively (Fig; 1). Therefore a conclusion may be drawn that the sp carbons are even more effective than sp² carbons in providing stability to the carboxylate anion. Therefore a higher Hammett's ρ value of 1.29 is observed in the dissociation equilibria of these acids. The Hammett's ρ value for these acid dissociation equilibria was calculated from only two pK_a values [8c]; 1.95 for X = 4-H and 2.13 for 4-CH₃. The Hammett's ρ point for this system has been shown separately in the figure 1.

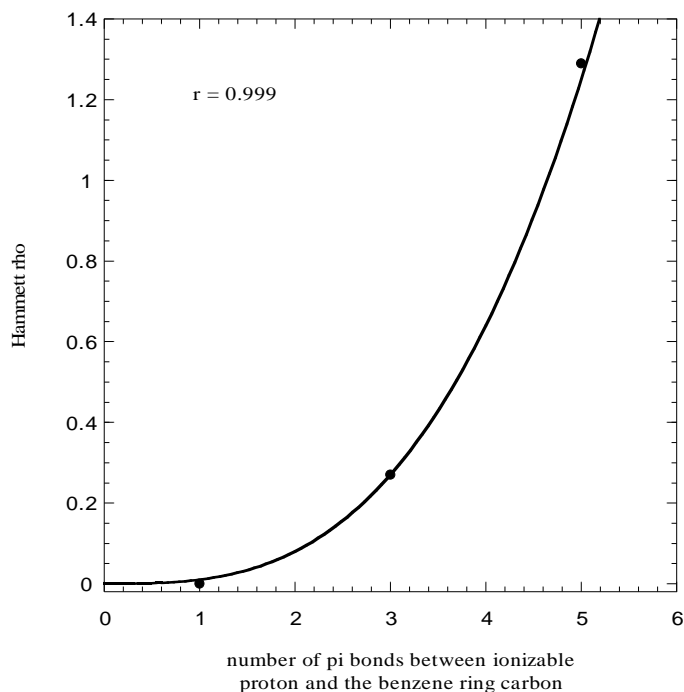
Further it is amazing to see a first-rate parabolic correlation (Fig. 3) between Hammett ρ versus number of π bonds according to the equation

$$\rho = (0.01) \cdot x^3$$

where 'x' is the number of π bonds (including the π bond of the carbonyl carbon of carboxylate group) between the ionizable proton and the benzene ring carbon of 5-phenyl-pentanoic acid ($\text{XC}_6\text{H}_4(\text{CH}_2)_4\text{COOH}$), 5-phenylpenta-2,4-dieoic acid ($\text{XC}_6\text{H}_4\text{CH}=\text{CH}-\text{CH}=\text{CHCOOH}$) and 5-phenylprop-2,4-diyneic acid ($\text{XC}_6\text{H}_4\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{COOH}$) dissociation equilibria.

As a conclusion what appears to be understood is the longer the side chain with sp³ carbons sooner the Hammett ρ approaches zero rapidly. But the presence of sp² or sp carbons overwhelmingly increases the Hammett ρ and makes the carboxylate anion very stable. It is also clear from the figures 1 and 2 that the decrease in Hammett ρ in the dissociation equilibria of benzoic acid, cinnamic acid, 5-phenylpenta-2,4-dieoic acid and 7-phenylhepta-2,4,6-trieoic acid is rather slow and it is due to a pair of sp² carbons and not by one single atom as predicted by Williams' equation [9].

Fig. 3: Plot of Hammett rho versus number of pi bonds between ionizable proton and the benzene ring carbon



Hence, appealing to reactivity-selectivity principle [11], it could be understood here that a less reactive and resonance delocalized carboxylate anions derived from cinnamic acids (Hammett $\rho = 0.47$), 5-phenylpenta-2,4-dieoic acids (Hammett $\rho = 0.27$) and 5-phenylprop-2,4-dienoic acids (Hammett $\rho = 1.29$) are more susceptible towards substituent effects and a more reactive and resonance localized carboxylate anions derived from phenyl propionic acids (Hammett $\rho = 0.22$) and 5-phenylpentanoic acids (Hammett $\rho = 0.00$) are less susceptible towards substituent effects.

ACKNOWLEDGEMENT

One of the authors (VJ) wishes to dedicate this manuscript to his Mentor Professor Dr. Steen Steenken of the then Max-Planck-Institut für Strahlenchemie, Mülheim-Ruhr, Germany.

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- [8] (a) The Hammett ρ value of 0.055 for this dissociation equilibrium 7 is an intelligent and reasonable estimate by the authors based on the argument that the decrease in Hammett ρ each time by a factor of close to two with increasing distance each time by a single carbon between the

reaction site and the benzene ring carbon and in turn the substituent. We could not find any Hammett ρ value for this dissociation equilibrium in literature. A search through SciFinder Scholar software, we could find that there is no change in individual pK_a values of $XC_6H_4CH_2CH_2CH_2CH_2COOH$ for $X = 4-H, 4-CH_3, 4-CH_3O, 4-CN$ and $4-Cl$. The pK_a values between 4.73 - 4.75. Hence Hammett ρ comes out to be zero. (b) A search through SciFinder Scholar software, we could find that there is no change in individual pK_a values of $XC_6H_4CH_2CH_2CH_2CH_2CH_2CH_2COOH$ for $X = 4-H, 4-CH_3O$ and $4-Cl$. The pK_a values for all the three acids were found 4.77. Hence Hammett ρ comes out to be zero. (c) A search through SciFinder Scholar software, we could find that the pK_a values of $XC_6H_4C\equiv C-C\equiv C-COOH$ 1.95 for $X = 4-H$ and 2.13 for $4-CH_3$.

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