Application of Hammett and Taft Equations Together on the Deprotonation Equilibriums of Isoxazolium Cations: A One Hour Graduate Classroom Teaching

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Abstract Hammett and Taft equations are applied together on the deprotonation equilibriums of isoxazolium cations.

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1. Introduction

Use of Hammett equation [1-4] dealing with *meta* and *para*-substituted benzene derivatives and Taft equation [5,6] dealing with *ortho*-substituted benzene derivatives in elucidating the reaction mechanisms in Physical-Organic Chemistry is indubitable. Since their introduction [1-6] numerous publications have appeared in literature [3,4] and are still being published to date. Application of Hammett and Taft equations to five membered aromatic heterocyclic ring systems was less commonly studied. The first application of Hammett law (not as an equation) [7] to furan ring was with 5-X-2-furoic acids [9]. But this was quoted in reference [10] as it was published in 1935 [11] even before the Hammett equation came into existence. In reference [10] by Freeman it is surprising to see even a Hammett ρ value was reported for the dissociation of 5-X-2-furoic acids without knowing Hammett σ values because evaluation of Hammett σ values took place only in 1937 [1]. Despite numerous research works on the application of Hammett and Taft equations to several organic reactions appeared in literature, their application to five membered ring systems did not find much place in chemistry research [9,12] except a one-page small publication appeared 50 years ago [10] and references cited therein. In this publication [10] the information of substituents in furan and thiophene derivatives used did not find a place. We have recently reported the application of Linear Free Energy Relationships (LFER) to the N(1)-H acidities of five membered nitrogen heterocyclic ring systems [13]. In the present work we have taken up the application of Hammett and Taft equations to deprotonation equilibriums of isoxazolium cations.

2. Methods

Linear correlation of pK_{aH} versus $\sum$(Hammett σ + Taft σ*) is done using the KaleidaGraph software, Reading, PA, USA. The chemical structures are drawn using ChemDraw software. Individual Hammett (σ) and Taft (σ*) substituent constants are from different sources [1-8]. The pK_{aH} values of isoxazolium cations are from reference [14]. Wherever the Taft σ* values are not available, they are calculated using the equation $\sigma^* = \frac{m + 0.106}{0.217}$, where σ$_m$ is the *meta*-substituent constant of that substituent [15]. And they were used in the summation of the Hammett and Taft substituent constants (column 3 and 4 in Table 1).

3. Results and Discussion

Visual observation of benzene and five membered heterocycles to look for the similarity of *para*, *meta* and *ortho*-carbons of benzene and 5th, 4th, and 3rd carbons of five membered 5 or 4- or 3-(X)-2-(Y)-heterocycles (as an example isoxazole with Z = O and V = N in the scheme 2 below for structure C):

As shown in scheme 1, it is known that all the six carbon atoms in the benzene ring are sp2 hybridized and benzene is a planar hexagon molecule.

Scheme 1

X = substtiuent

Y = -functional group

Z and V = hetero atoms
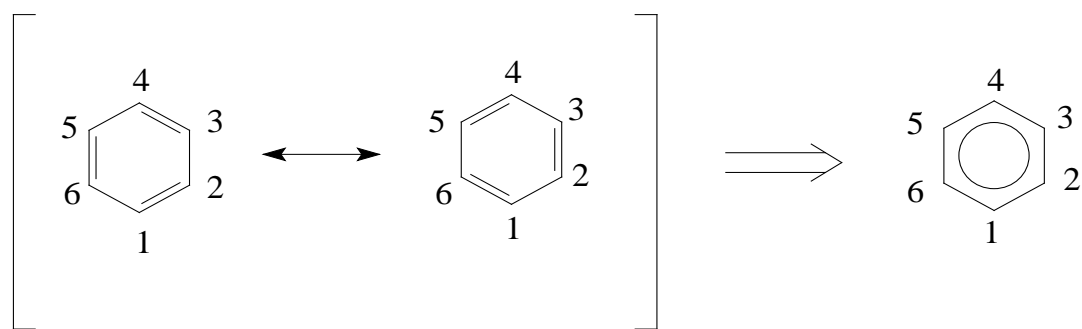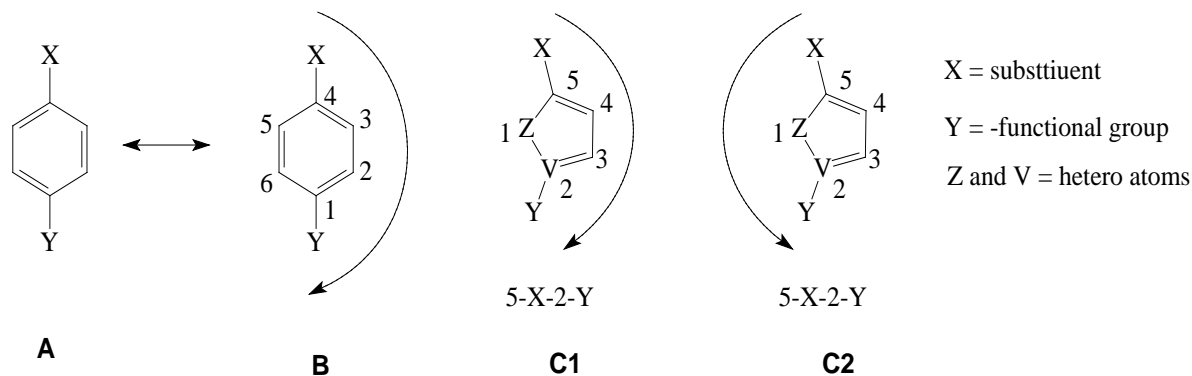
Scheme 2

This explains an equal possibility for the formation of C1 - C2, C3 - C4, C5 - C6 π bonds or C2 - C3, C4 - C5, C6 - C1 π bonds. The hybrid structure is represented by inserting a circle in the ring as shown above in scheme 1. Hence, it explains the formation of two resonance structures proposed by Kekule [16] and they will always be in dynamic equilibrium. At any given point of time during the dynamic equilibrium process of benzene, the statistical percentage of existence of either **A** or **B** in scheme 2 is 50:50.

Now comparing the structure, **A** or **B** and the structure of the 5-X-2-Y-heterocycle **C1** of scheme 2, the functional group Y and the substituent X are separated by one single bond and two double bonds or simply by two pairs of π-electrons or by two sp2 carbons in benzene ring **B** and the heterocycle **C1**. Therefore, it can be assumed that the substituent electronic effects can be transmitted from carbon 4 bearing the substituent X to the functional group Y at carbon 1 of the **benzene**. This kind of situation of the structure **C1** where in the substituent electronic effects can be transmitted from carbon 5 bearing the substituent X to the functional group Y at carbon 2 of the heterocycle would be just like that of structure **A** or **B**. Therefore carbon 5 of the structure **C1** of scheme 2 could best be assumed as a *para*-carbon. The transmittance of substituent effect from carbon 5 to the deprotonation site (=HN⁺-) via oxygen is also likely, for reasons, though the hybridization of oxygen is in between sp2 and sp3 having lot more towards sp3 because the bond angle of ∠CON was reported as 108.8 determined by microwave spectroscopy and it is not much away from 109.5, the

tetrahedral angle [17]. There is a very recent review article on hybridization which narrates nicely the relation between bond angle index and the quantity sp^m hybridization character [18]. And the angle of ∠CON of 108.8 which is little less than the typical tetrahedral angle of 109.5 led to evaluate the hybridization of oxygen and it gave a small fraction $\left(\dfrac{109.5 - 108.8}{109.5}\right) \text{X}100 = 0.64\%$ of sp2 character, due to this the transmittance of substituent effect via oxygen cannot completely be ruled out as shown in structure **C2** of scheme 2.

Similarly, now comparing the structure **E** and the structure of the 4-X-2-Y-heterocycle **F1** of scheme 3, the functional group Y and the substituent X are separated by one single bond and one double bond or simply by a pair of π-electrons or by one sp2 carbon. It can be assumed that the substituent electronic effects can be transmitted from carbon 3 bearing the substituent X to the functional group Y at carbon 1 of the **benzene**. This kind of situation of the structure **F1** where in the substituent electronic effects can be transmitted from carbon 4 bearing the substituent X to the functional group Y at carbon 2 of the heterocycle would be just like that of structure **E**. Therefore, the carbon 4 of the structure **F1** could best be assumed as a *meta*-carbon. Also, like above the transmittance of substituent effect via oxygen cannot completely be ruled out as shown in structure **F2** of scheme 3.

Again, similarly the carbon 3 of the structure **I** could best be assumed as an *ortho*-carbon as shown in scheme 4.
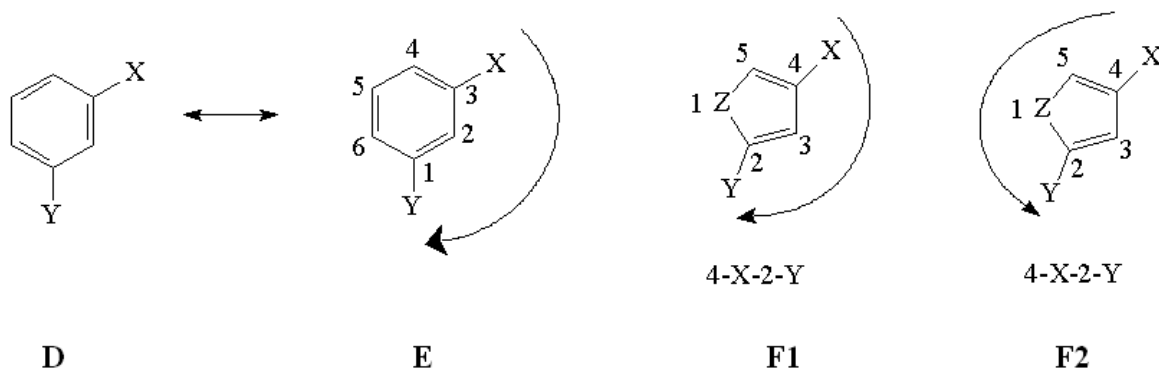
Scheme 3
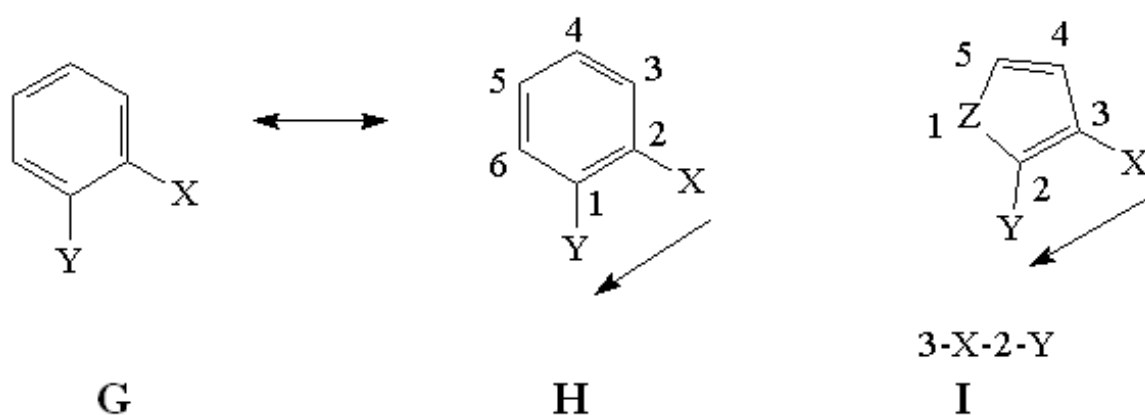
Scheme 4

In fact, molecular orbital calculations, and dipole moment data of 2-X-thiophene carboxylic acids suggested that the *para, meta* and *ortho* carbons of benzene correspond to 5, 4 and 3 carbons of the 5 membered heterocycle [19,20]. From the correlation of carbon-13 chemical shifts versus 1H-proton chemical shifts, in which the striking parallelism of the resonance shifts of the benzene and five membered heterocycle nuclei, implies that the resonances of both nuclei respond in a parallel way to the local π-electron density on the carbon atom [21]. And as such five membered heterocycles with one or two heteroatoms are planar pentagons. They have sp2 hybridized carbon atoms. They possess significant aromatic character resulting from the lone pair of electrons of the hetero atom/s and the two pairs of carbon π electrons.

Now applying the above said observations to isoxazolium cations: The substituents are assumed at position 3 as *ortho*-substituents, at position 4 as *meta*-substituents and at position 5 as *para*-substituents. And for disubstituted and trisubstituted isoxazoles the corresponding summed-up [$\sum$(Hammett σ + Taft σ*)] values are taken. Reasonably a good straight line is obtained (Figure 1). Though the correlation coefficient is a little poor (R = 0.8074), the trend is unmistakable. And another striking and important explanation for a little poor correlation of Hammett-Taft plot is: Isoxazole is aromatic but not as aromatic as benzene. The lone pair of oxygen does not participate effectively in resonance because oxygen being more electronegative. As a result, the isoxazole ring cannot maintain an effective uninterrupted delocalization of its π-electrons to have a continuous conjugation like that in benzene.
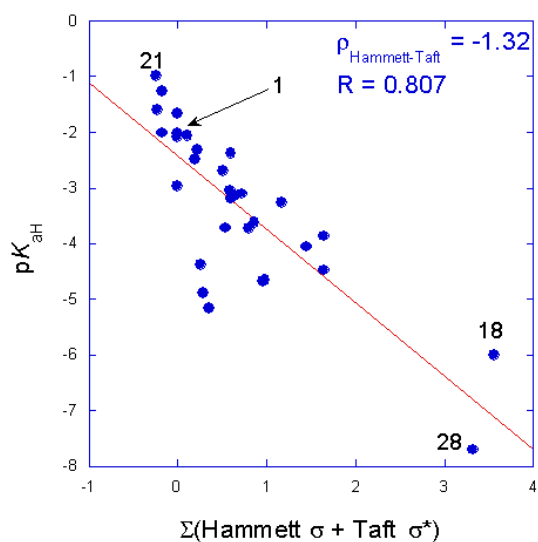
And the substituents are assumed at position 3 as *ortho*-substituents as above, at position 4 as *para*-substituents and at position 5 as *meta*-substituents for the transmittance via oxygen. Figure 2 is the Hammett-Taft plot for the transmittance via oxygen. And for both types of transmittance the corresponding substituent constants are calculated and are given in column 3 and 4 respectively of Table 1.

4. Conclusions

The slopes i. e. the $\rho_{Hammett-Taft}$ = **-1.32** and **-1.43** from the plots should be read as positive value since the plots are made pK_{aH} versus $\sum$(Hammett σ + Taft σ*) substituent constants. The positive $\rho_{Hammett-Taft}$ values indicate that electron withdrawing substituents increase the deprotonation and electron donating substituents decrease the deprotonation.

Table 1. $\sum$(Hammett σ + Taft σ*) values and pK_{aH} data of isoxazolium cations

Sl. No.	X	$\sum$(Hammett σ + Taft σ*)	$\sum$(Hammett σ + Taft σ*) (Assuming substituent effect via oxygen)	pK_{aH}
1	H	0.00	0.49	-2.03
2	3-Me	0.00	0.00	-1.67
3	5-Me	-0.17	-0.07	-2.01
4	3-Ph	0.60	0.06	-3.19
5	5-Ph	-0.01	0.06	-2.96
6	3-(4-NO$_2$C$_6$H$_4$)	1.64	1.64	-4.48
7	5-(4-NO$_2$C$_6$H$_4$)	0.26	0.25	-4.39
8	3,5-diMe	-0.17	-0.07	-1.26
9	3-Me-5-Ph	-0.01	0.06	-2.08
10	5-Me-3-Ph	0.43	0.53	-2.38
11	3,5-diPh	0.59	0.54	-3.05
12	3-(4-Cl-C$_6$H$_4$)-5-Ph	1.18	1.23	-3.26
13	3-(3-NO$_2$-C$_6$H$_4$)-5-Ph	1.46	1.52	-4.05
14	3-(4-NO$_2$-C$_6$H$_4$)-5-Ph	1.64	1.69	-3.87
15	5-(4-Cl-C$_6$H$_4$)-3-Ph	0.72	0.75	-3.10
16	5-(3-NO$_2$-C$_6$H$_4$)-3-Ph	0.81	0.82	-3.73
17	5-(4-NO$_2$-C$_6$H$_4$)-3-Ph	0.85	0.84	-3.63
18	3-Cl-5-Ph	3.56	2.90	-6.01
19	4-Cl-5-Ph	0.36	0.43	-5.16
20	5-Cl-3-Ph	0.29	0.43	-4.90
21	3,4,5-triMe	-0.24	-0.24	-1.00
22	4-Me-3,5-diPh	0.52	-0.11	-2.70
23	3,4,5-triPh	0.65	0.72	-3.14
24	3,5-diMe-4-Cl	0.20	0.16	-2.48
25	3,5-diMe-4-Br	0.22	0.16	-2.32
26	3,5-diMe-4-I	0.11	0.21	-2.06
27	3,5-diMe-4-NO$_2$	0.54	0.71	-3.72
28	3,4-diCl-5-Ph	3.32	3.25	-7.70
29	4-Cl-3,5-diPh	0.96	0.89	-4.68
30	4-Br-3,5-diPh	0.98	0.91	-4.67
31	3,5-diMe-4-PhCH$_2$	-0.25	0.39	-1.60

Figure 1. Plot of pk_{aH} vs $\sum$(Hammett σ + Taft σ*)
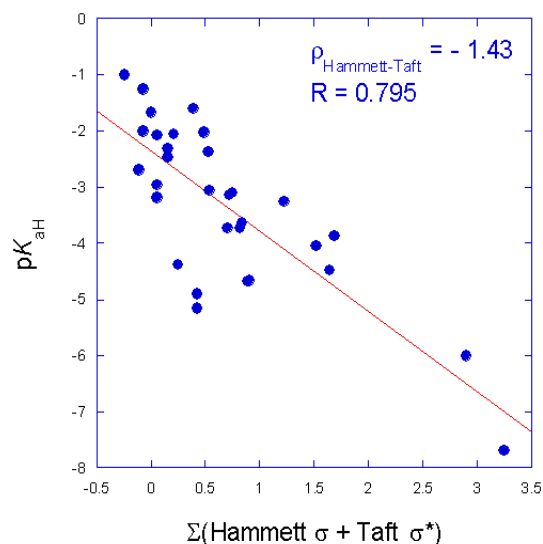
Figure 2. Plot of pk_{aH} vs $\sum$(Hammett σ + Taft σ*)

The Hammett-Taft plots are shown in figures 1 and 2.
The authors don't have any conflict of interest.

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