Attenuation Effect in Twenty One Different Proton Dissociation Equilibriums Brought on One Rope: A Chemical Education Tool for Evaluation of pK_a of Proton Dissociation Equilibrium of Any Substituted Benzene (XC$_6$H$_5$)

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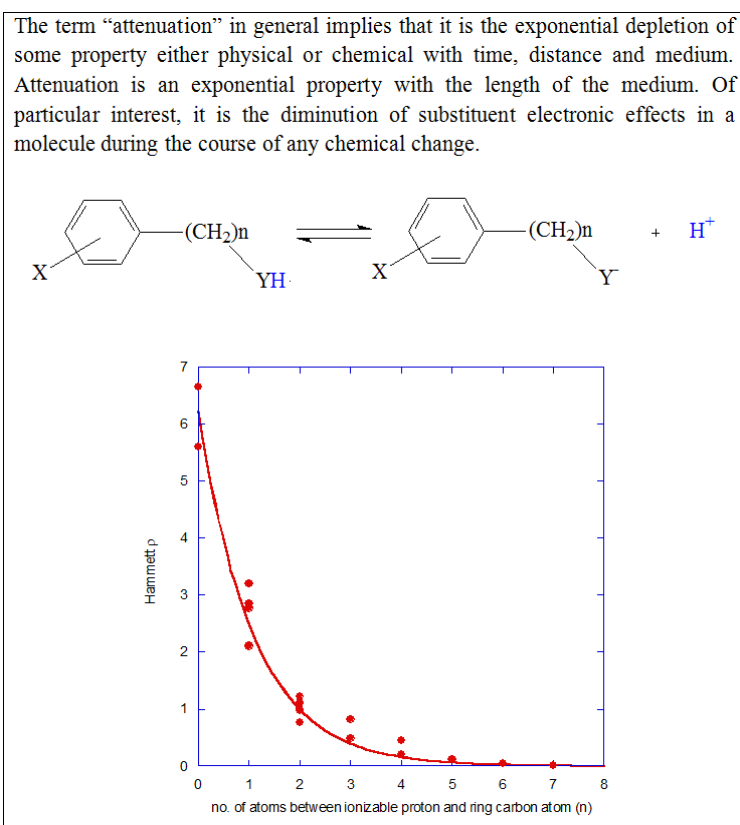[1]Department of Chemistry, Geethanjali College of Engineering and Technology, Cheeryal-501301, Telangana, India
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Abstract The strong empirical relation, $\rho = (2.4)^{(2-i)}$, between the Hammett ρ for proton dissociation of several acids and the number, "*i*", of atoms between the ionizable hydrogen and the ring carbon (Andrew Williams, Free Energy Relationships in Organic and Bioorganic Chemistry, Royal Society of Chemistry, Cambridge, 2003, p. 75) is used to construct a graph for twenty one different proton dissociation equilibriums. The plot of Hammett ρ versus number of atoms *i* between ionizable hydrogen and the ring carbon atom is observed to be an excellent exponential-decay locus. A good average and intelligent value of Hammett ρ is obtained for the benzene dissociation equilibriums by interpolating the locus of the correlation on to Y-axis. Using this Hammett ρ value and the Hammett equation log $[(K_a)_X / (K_a)_H] = \rho\sigma$, the p$K_a$ value can be calculated for any substituted benzene knowing the pK_a value of benzene to be 43. The points for proton dissociation equilibriums of phenylethyl ammonium ions and benzyl alcohols deviated from the graph hence not included in the correlation. Possible explanations are given for deviation of these two equilibriums.

Graphical abstract

The term "attenuation" in general implies that it is the exponential depletion of some property either physical or chemical with time, distance and medium. Attenuation is an exponential property with the length of the medium. Of particular interest, it is the diminution of substituent electronic effects in a molecule during the course of any chemical change.

1. Introduction

A considerable interest on the application of attenuation effect due to methylene group was gained from our laboratory [1,2,3,4]. The emergence of Andrew Williams' strong empirical relation [5] based on the existence of attenuation effect, systematically observed in the study of acid dissociation equilibriums of benzoic acids, phenyl acetic acids and phenyl propionic acids is a successful achievement. The same was extended to aromatic [1,2], and aliphatic [3,4] systems from our laboratory. This empirical relation [5] is further made use in the present work to bring twenty one different proton dissociation equilibrium reactions on one rope. A good average and intelligent value of Hammett ρ is obtained for the benzene dissociation equilibriums by interpolating the locus of the correlation on to Y-axis. And this study is extended to calculate pK_a values using the Hammett equation log $[(K_a)_X / (K_a)_H] = \rho\sigma$, for any substituted benzenes knowing the pK_a value of unsubstituted benzene to be 43.

2. Methods

All calculations and curve fittings were done by Kaleida Graph software version 4.1 supplied by Synergy Software INC., Reading, PA, USA. All chemical structures were drawn using "Chemdraw" software.

3. Discussion

First let us see the dissociation equilibriums of different acids with increasing length of carbon chain between ionizable hydrogen and the ring carbon/nitrogen atom. Table 1 narrates twenty one different proton dissociation equilibrium reactions with Hammett ρ values, and the number of atoms between ionizable hydrogen and the ring carbon/nitrogen. The Hammett ρ values are given in the increasing order down to the table. Using the Williams' equation 1

$$\rho = (\mathbf{m_1})^{(\mathbf{2-i})} \qquad (1)$$

where m_1 is an arbitrary constant, a plot of Hammett ρ versus number of atoms between ionizable hydrogen and ring carbon is made and shown in Figure 1. From equation 1 it is clear that if i = 0, i.e. if there are no atoms between the ionizable hydrogen and the ring carbon atom, the example would be benzene itself. Then the Hammett ρ value would be $m_1^{(2-i)} = m_1^{(2-0)}$. Here, from the curve fit of the data, m1 was found to be 2.4917 (see box in the figure). Therefore the Hammett ρ value for proton

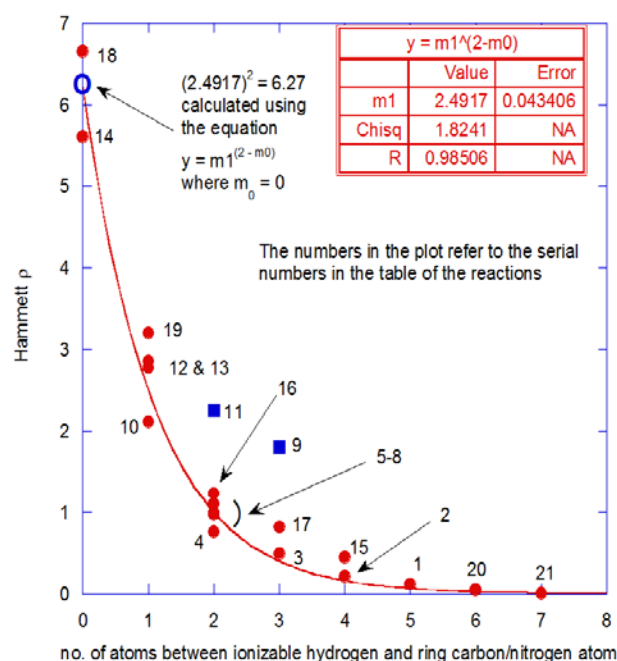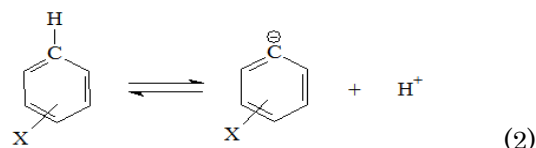dissociation equilibrium (equation 2) of benzene will be $(2.4917)^2 = 6.27$.

$$(2)$$

Figure 1. Plot of Hammett ρ versus number of atoms (m_0) between ioniable hydrogen and the ring carbon atom
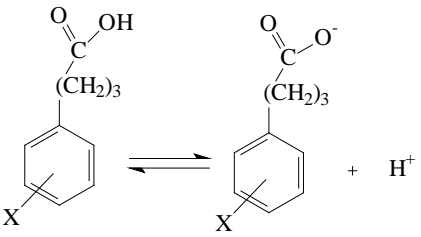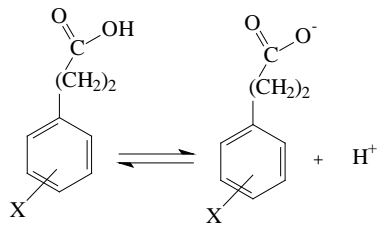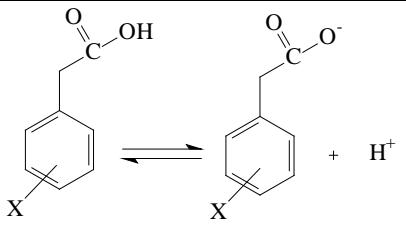
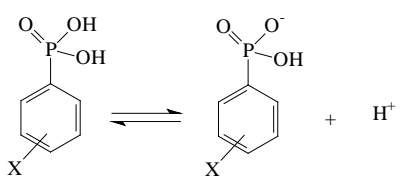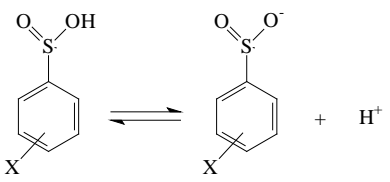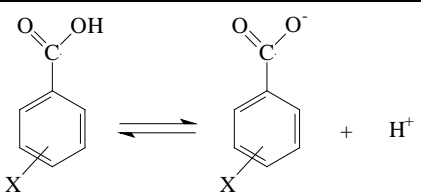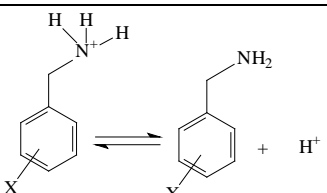And this value is very close to the average (5.6 + 6.6 = 12.2 /2 =6.1) of the two values previously reported, one for proton dissociation equilibrium of benzene[1] and the other proton dissociation equilibrium of pyridinium ions [2] (equation 3). In both the cases "*i*", number of

$$(3)$$
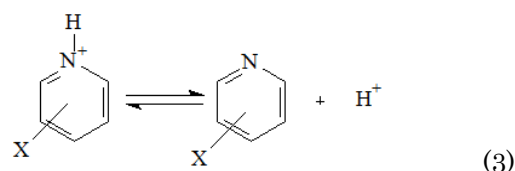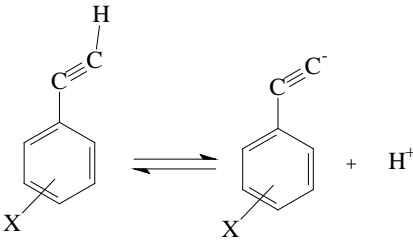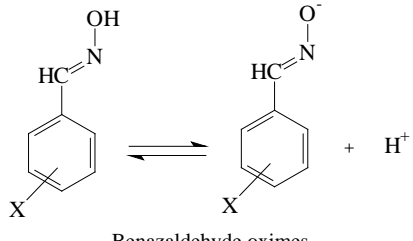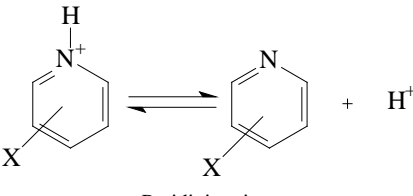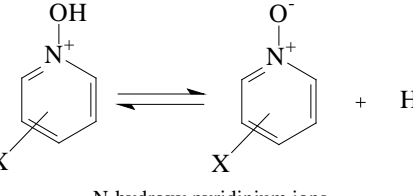
atoms between ionizable hydrogen and ring carbon/ nitrogen is zero.

But the points of the equilibriums of the compounds 9 and 11 deviated from the correlation. The deviation could be due to the anomalous Hammett ρ obtained from the anomalous pK_a values of phenylethyl ammonium ions [6]. The anomalistic pK_a values are due to the formation of the more stable zwitter ion of 4-hydroxy phenylethyl ammonium ion and even more stabilization of the 3, 4-dihydroxy phenylethyl ammonium ion due to hydrogen bonding, both are as shown below (equations 4 and 5)

Table 1. Different acid dissociation equilibriums, Hammett ρ values, and the number of atoms between ionizable proton and the ring carbon

Sl. no.	Dissociation equilibrium	Hammett ρ At 25°C in H_2O	No. of atoms between ionizable hydrogen and ring carbon	Notes and references
1	Phenyl butyric acids	0.12	5	a
2	Phenyl propionic acids	0.21	4	b
3	Phenyl acetic acids	0.49	3	b
4	Phenyl phosphonic acids	0.76	2	b
5	Phenyl sulfinic acids	0.98	2	c
6	Benzoic acids	1.00	2	d
7	Benzyl ammonium ions	1.10	2	e

8	Phenyl sulfonic acids	1.11	2	f
9	Phenyl ethyl ammonium ions	1.8	3	g
10	Phenols	2.11	1	b
11	Benzyl alcohols	2.25	2	h
12	Anilinium ions	2.77	1	b, i
13	Thiophenols	2.85	1	j
14	Benzenes	5.6	0	h
Molecules with unsaturated side chain				
15	Cinnamic acids	0.45	4	b

|				
16	 Phenyl acetylenes	1.23	2	k
17	 Benazaldehyde oximes	0.82	3	l
	Molecules with hetero atoms in the benzene ring (pyridine derivatives)			
18	 Pyridinium ions	6.65	0	m
19	 N-hydroxy pyridinium ions	3.20	1	n
	Aliphatic molecules			
20	$X(CH_2)_4COOH \rightleftharpoons X(CH_2)_4COO^- + H^+$ Pentanoic acids	0.05	6	o
21	$X(CH_2)_5COOH \rightleftharpoons X(CH_2)_5COO^- + H^+$ Hexanoic acids	0.008	7	p

Notes and references:

[a] from J. Deles, B. Szechner, *Roczniki Chemii*, 45, 1243 (1971); [b] from reference 7; [c] from C. D. Ritchie, J. D. Saltiel and E. S. Lewis, J. Am. Chem. Soc., 83, 4601, 1961; [d] from L. P. Hammett, Physical Organic Chemistry, McGraw-Hill, New York, 1940, pp. 184-189; [e] Calculated from the plot of pK_a versus Hammett σ. The pK_a values are from L. F. Blackwell, A. Fischer, I. J. Miller, R. D. Topsom and J. Vaughan, *J. Chem. Soc.,* pp. 3588, (1964); [f] Calculated from the pK_a values of phenyl sulfonic acid (-2.8), *https://en.wikipedia. org/wiki/Benzenesulfonic acid* and 4-nitrophenylsulfonic acid (-2.9) http://foodb.ca/ compounds/FDB023939; [g] Reference 6; [h] from V. Jagannadham, *Bulgarian Chemical Communications,* Volume 41, Number 1 (pp. 50-53) 2009; [i] Calculated from the plot of p*Ka* versus Hammett σ, The p*Ka* values are from Brown, H.C. et al., in Braude, E.A. and F.C. Nachod, *Determination of Organic Structures by Physical Methods*, Academic Press, New York, 1955; [j] Calculated from the plot of pK_a versus Hammett σ, The pK_a values are from Kevin N. Dalby and William P. Jencks, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1555-1564; [k] Hammett ρ for this dissociation equilibrium in water is obtained by multiplying the Hammett ρ of this reaction in methanol 0.85 (From M.S. thesis of Eric T. Lloyd, Department of Chemistry, University of Missouri Rolla, USA, 1976) with Hammett ρ of 1.45 of benzoic acids in methanol (Halina Bartnika, Irena Ojanowska and Marek K. Kalinowski, *Aust. J. Chem.*, 1993, 46, 31-36); [l] From O. L. Brady and N. M. Chukshi, *J. Chem. Soc.*, p 2946, 1929, O. L. Brady and R. F. Goldstein, *J. Chem. Soc.*, p 1918, 1926; [m] Hammett ρ is obtained from the pK_a versus σ plot. pK_a values are from H. H. Jaffe and G. O. Doak, *J. Am. Chem. Soc.* 77, pp. 4441, (1955) and K. Clarke and K. Rothwell, *J. Chem. Soc.*, 1885, 1960; [n] Hammett ρ is obtained from the pK_a versus σ plot. pK_a values are from H. H. Jaffe and G. O. Doak, *J. Am. Chem. Soc.* 77, pp. 4441, (1955); [o] first Taft ρ* is calculated taking X = H (pK_a = 4.82, https://en.wikipedia. org/wiki/Valeric_acid) and X= CH₃ (pK_a = 4.88, https://en.wikipedia.org/wiki/Hexanoic _acid), then multiplied by 2.48 to convert on to Hammett scale to get Hammett ρ. [p] similarly first Taft ρ* is calculated taking X = H (pK_a = 4.88, https://en.wikipedia.org/wiki/ Hexanoic_acid and X = CH₃ (pK_a = 4.89, https://www.chemicalbook.com/ChemicalProduct PropertyENCB7852833.htm, then multiplied by 2.48 to convert on to Hammett scale to get Hammett ρ.

$$(4)$$

and

$$(5)$$
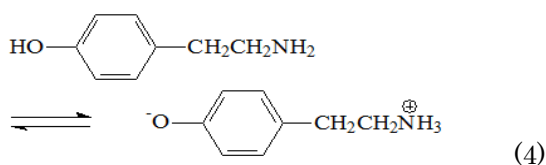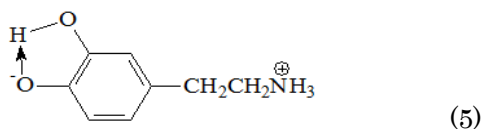
The anomalous Hammett ρ obtained from the proton dissociation equilibrium of benzyl alcohols is due to: the Hammett ρ value for benzyl alcohols dissociation equilibriums should be simply 1.11 [7], which is half of that of phenoxide ion equilibriums, based on the fact that the Hammett ρ value for phenyl acetic acids has become reduced to half of that of benzoic acids 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 [8]. One putative explanation of this, offered by Wiberg [9], 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 (Equation. 6) to contribute towards higher Hammett ρ value.

$$(6)$$
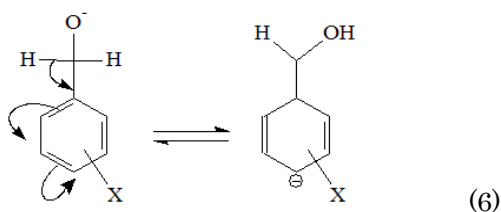
Calculation of pK_a *of any substituted benzene:* The Hammett ρ for the proton dissociation equilibriums (equation 2) from the present work is 6.27. And the Hammett equation is:
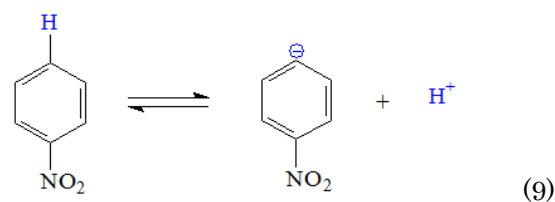
$$log\left[\left(K_a \right)_X / \left(K_a \right)_H \right] = \rho\sigma \qquad (7)$$

Rewriting this equation in terms of pK_a we get

$$\left(pK_a \right)_H - \left(pK_a \right)_X = \rho\sigma \qquad (8)$$

$(pK_a)_H$ of benzene is 43 [10], Hammett ρ is 6.27 and if the $(pK_a)_X$ of nitrobenzene (for X = NO_2) is to be calculated, assuming the 'the hydrogen" para to nitro

group in benzene ring is to be deprotonated as shown in equation 9, then σ for 4-NO_2 substituent has to be taken as 0.78 [7].

$$(9)$$

Substituting these values in equation 8

$$43 - \left(pK_a \right)_{4-NO_2} = 6.27 \times 0.78$$

$$\left(pK_a \right)_{4-NO_2} = 43 - 4.89 = 38.1$$

Therefore the pK_a of nitrobenzene with deprotonation at *para* position is 38.1. Similarly for any substituted benzene the pK_a values could be calculated.

References

[1]   Jagannadham V 2009 The attenuation effect through methylene group. *Bulgarian Chem. Commns*. **41** 50

[2]   Sanjeev R, Jagannadham V and Veda Vrath R 2014 Attenuation effect through methylene group: Part II, *Bulgarian Chem. Commns*. **46** 375

[3]   Sanjeev R and Jagannadham V 2017 Estimation of Taft ρ^* of dissociation equilibriums of methanium ions RCH_4^+ the hydrocarbon super acids: a chemical education practice in physical-organic chemistry class-room, *Current Physical Chemistry* **7** 218

[4]   Sanjeev Rachuru, Jagannadham Vandanapu and Sreedhar Pandiri, Tetrahedral Nature Determines the Stability of Reactive Intermediates: A Chemical Education Perspective, *Oriental J. Chemistry*, 2019 (in press)

[5]   A. Williams, Free Energy Relationships in Organic and Bioorganic Chemistry, Royal Society of Chemistry, Cambridge, 2003, p. 75

[6]   Hammett ρ is calculated from the plot of pK_a versus Hammett σ values of only 4-H, 4-OH and 3-OH substituted phenyl ethyl ammonium ions. pK_a values are from Murray M. Tuckerman, J. Richard Mayer and Frederick C. Nachod, *J. Am. Chem. Soc.*, **1959**, *81*, 92

[7]   H. H. Jaffe, *Chem. Rev*, **53**, 191 (1953)

[8]   The ρ value for this equilibrium is an estimate based on the correlation of gas-phase ΔH_{acid} values[9] of different oxygen containing acids and is done as follows: The Hammett ρ value for phenol dissociation equilibriums in aqueous solution is 2.21[7]. The gas-phase ρ value for this same equilibrium is 1.28[9]. 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[9]. Therefore the Hammett ρ value for benzyl alcohols dissociation equilibriums 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.

[9]   K. B. Wiberg, *J. Org. Chem.,* **68**, 875 (2003)

[10] E. P. Serjeant and B. Dempsey (eds.), *Ionization Constants of Organic Acids in Solution*, IUPAC Chemical Data Series No. 23, Pergamon Press, Oxford, UK, 1979.