Comparison of Substituent Effects in Benzenes (XC₅H₅C), Pyridines (XC₅H₄N) and Phosphorines (XC₅H₄P) and their Protonated Species

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Abstract
Collection of interesting and stimulative data led us to construct Hammett plots for different properties like proton affinities, gas phase basicities, solvation free energies of free and protonated benzenes (I), pyridines (II) and phosphorines (III), and for pKₐ values of protonated pyridines and phosphorines. Trends in Hammett reaction constants (ρ) for all these processes were discussed.

Keywords: benzenes, pyridines, phosphorines, pKₐ, proton affinities, gas phase basicities, solvation free energies

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1. Introduction
Acuity of work in chemical education and chemical research that took a shape from literature reported data on several chemical and physical aspects like phase transition temperatures, dipole moments, surface tensions, attenuation effect, associative and non-associative behavior of liquids, stability and lifetimes of reactive intermediates, LFER, effect of hybridization of carbon on Hammett (ρ) and Taft (ρ*) reaction constants, prediction of pKₐ values of unstable arenium ions and benzenes, from our group has been ever increasing in recent times [1-63]. In the present work to go a step ahead we have tried the comparison of substituent effects on pKₐ, proton affinities, gas phase basicities, solvation free energies in benzenes (C₅H₆C), pyridines (C₅H₅N) and phosphorines (C₅H₅P) and their protonated species.

2. Methods
All the linear correlations were done using the KaleidaGraph software, Reading, PA, USA. All chemical structures were drawn using chemdraw software. All Hammett σ values are from reference 64.

3. Discussion
Hammett reactions constants (ρ) and pKₐ data of arenium, pyridinium and phosphorinium ions are given in Table 1. The corresponding plots are shown in Figure 1, Figure 2 and Figure 3.

Since the Hammett ρ can not be determined for the dissociation equilibriums of arenium ions X₅C₆H₅⁺ ⇌ X₅C₆H₄⁺ + H⁺ as they are highly unstable, an alternate and lucid method was adopted by us based on the attenuation effect [26]. Figure 1 shows the determination of the Hammett ρ for the dissociation equilibriums of arenium ions X₅C₆H₅⁺ ⇌ X₅C₆H₄⁺ + H⁺ from the study of attenuation effect of methylene group (-CH₂-) on the dissociation equilibriums of anilinium ions, benzyl ammonium ions and 2-phenylethyl ammonium ions [26] and using the Andrew Williams’ empirical equation ρ = ml^12 - 0.016 [65] where m₁ is an arbitrary constant “i” is the number of atoms between ionizable proton and the ring carbon.
Table 1. pKₐ values of pyridinium and phosphorinium ions and Hammett ρ values for the three equilibriums

| Sl. No. | X       | Hammett σ | pKₐ⁽ᵃ⁾ |
|---------|---------|-----------|--------|
|         | H       | 0.00      | 5.21   |
|         | 3-F     | 0.34      | 2.93   |
|         | 3-Cl    | 0.37      | 3.45   |
|         | 4-Cl    | 0.23      | 4.52   |
|         | 4-Me    | -0.17     | 7.21   |
|         | 4-MeO   | -0.27     | 8.19   |
|         | 3-Me    | 0.07      | 5.70   |
|         | 4-NH₂   | -0.66     | 9.20   |
|         | 4-Et    | -0.16     | 6.00   |
|         | 4-Me    | -0.17     | 6.00   |

Hammett ρ for this equilibrium is 14.3 determined from the attenuation effect (Reference 26)

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

Figure 2. Plot of pKₐ vs Hammett σ for pyridinium ions

Figure 3. Plot of pKₐ vs Hammett σ for phosphorinium ions

The negative Hammett ρ values for the equilibriums X₅C₅H₅N⁺ ⇌ X₅C₅H₄N + H⁺ and X₅C₅H₅P⁺ ⇌ X₅C₅H₄P + H⁺ are from the plots of pKₐ versus Hammett σ to be taken as positive for the plots of log Kₛ (since -log Kₛ = pKₐ) versus Hammett σ. Therefore the three Hammett ρ values of the three equilibrium reactions are 14.3, 6.48 and 7.73 respectively. It is to be noted that there is a large difference of nearly 7.8 and 6.6 units between Hammett ρ of the equilibrium X₆C₆H₆⁺ ⇌ X₆C₆H₅ + H⁺ and of the equilibriums of X₅C₅H₅N⁺ ⇌ X₅C₅H₄N + H⁺ and X₅C₅H₅P⁺ ⇌ X₅C₅H₄P + H⁺. This is mainly due to the loss of energy of the highly unstable and energetic...
intermediate arenium ions to drive back to the highly stable and less energetic benzene molecule. And this involves the restoration of the aromaticity due to the relief of unit positive charge on the arenium ions. And this small difference of 1.25 units of Hammett \( \rho \) between the equilibriums of \( \text{XC}_5\text{H}_5\text{N}^+ \rightleftharpoons \text{XC}_5\text{H}_4\text{N} + \text{H}^+ \) and \( \text{XC}_5\text{H}_5\text{P}^+ \rightleftharpoons \text{XC}_5\text{H}_4\text{P} + \text{H}^+ \) is due to only the difference of the occupancy of the lone pairs of electrons of N and P. The lone pair of electrons of N is in the p orbital and that of P is in the d orbital. In spite of the fact that the p orbital is more electronegative than d orbital the tendency towards retention of aromaticity of both the molecules even on protonation is a prime reason. There are several arguments about the aromaticity of phosphorine based on many theoretical calculations. And it is believed to have the 88-96% of aromaticity of that of benzene [67]. Such a high aromaticity of phosphorine is reflected from the well matched electronegativities of phosphorous (2.1) and carbon (2.5) [67].

Hammett reactions constants (\( \rho \)) and proton affinity data of benzenes, pyridines and phosphorines are given in Table 2. The corresponding Hammett plots are shown in Figure 4, Figure 5 and Figure 6.

Figure 4 shows the determination of the Hammett \( \rho \) for the proton affinities (PA) of benzenes from the plot of PAs versus Hammett \( \sigma \).

Figure 5 shows the determination of the Hammett \( \rho \) for the proton affinities (PA) of pyridines from the plot of PAs versus Hammett \( \sigma \).

Figure 6 shows the determination of the Hammett \( \rho \) for the proton affinities (PA) of phosphorines from the plot of PAs versus Hammett \( \sigma \).

Table 2. Hammett reaction constants (\( \rho \)) and proton affinity data of benzenes, pyridines and phosphorines

| Sl. No. | X     | Hammett \( \sigma \) | PA (k.cals.mol\(^{-1}\)) | pyridine | Hammett \( \sigma \) | PA\(^{\prime}\) (k.cals.mol\(^{-1}\)) | phosphorine | Hammett \( \sigma \) | PA\(^{\prime}\) (k.cals.mol\(^{-1}\)) |
|--------|-------|-------------------|-----------------|----------|--------------------|-----------------|-------------|--------------------|-----------------|
| 1      | 4-NH\(_2\) | -0.66             | 209 212         | H        | 0.00               | 223.4           | H           | 0.00               | 195.6           |
| 2      | 4-MeO  | -0.27             | 199 202         | 3-F      | 0.34               | 216.3           | 4-F         | 0.06               | 190.7           |
| 3      | 4-CHO  | 0.22              | 199 -           | 4-Cl     | 0.37               | 217.5           | 4-Cl        | 0.23               | 191.5           |
| 4      | 4-CN   | 0.66              | 195 170         | 4-CN     | 0.23               | 220.0           | 4-NO\(_2\)  | 0.80               | 181.0           |
| 5      | 4-OH   | -0.37             | 195 197         | 4-Me     | -0.07              | 228.1           | 4-Me        | -0.17              | 199.4           |
| 6      | 4-NO\(_2\) | 0.80            | 193 165         | 4-MeO    | -0.27              | 231.4           | 4-CF\(_3\)  | 0.54               | 185.9           |
| 7      | 4-Et   | -0.15             | 191 -           | -        |                    |                 | -           |                    |                 |
| 8      | 4-Me   | -0.17             | 190 192         | -        |                    |                 | -           |                    |                 |
| 9      | H      | 0.00              | 184 183         | -        |                    |                 | -           |                    |                 |
| 10     | 4-F    | 0.06              | 183 183         | -        |                    |                 | -           |                    |                 |
| 11     | 4-Cl   | 0.23              | 183 184         | -        |                    |                 | -           |                    |                 |
| 12     | 4-CF\(_3\) | 0.54            | 171             | -        |                    |                 | -           |                    |                 |
| 13     | 4-SiH\(_3\) | 0.10           | 185             | -        |                    |                 | -           |                    |                 |
| 14     | 4-PH\(_2\) | 0.05            | 191             | -        |                    |                 | -           |                    |                 |
| 15     | 4-SH   | 0.15              | 196             | -        |                    |                 | -           |                    |                 |

\(^{\text{a}}\)Yan K. Lau and Paul Kebarle, J. Am. Chem. Soc. 1976, 98, 23, 7452-7453, https://doi.org/10.1021/ja00439a072.

\(^{\text{b}}\)from Pham-Cam Nam, and Minh Tho Nguyen, Asit K. Chandra, J. Phys. Chem. A 2006, 110, 4509-4515.

\(^{\text{c}}\)from reference 65.

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**Figure 4.** Plot of PAs vs Hammett \( \sigma \) for benzenes

**Figure 5.** Plot of PAs versus Hammett \( \sigma \) for pyridines
Hammett \( \rho = -20.1 \), \( R = 0.9600 \)

Hammett \( \rho = -32.0 \), \( R = 0.9498 \)

Hammett \( \rho = -21.7 \), \( R = 0.9857 \)

Hammett \( \rho = -20.2 \), \( R = 0.9602 \)

**Figure 6.** Plot of PAs versus Hammett \( \sigma \) for phospherines

**Figure 7.** Plot of \(-\Delta G^\circ\) vs Hammett \( \sigma \) for benzenes

**Figure 8.** Plot of gas phase basicities (GB) vs Hammett \( \sigma \) for pyridines

**Figure 9.** Plot of gas phase basicities (GB) vs Hammett \( \sigma \) for phospherines

| Sl. No. | X    | Hammett \( \sigma \) | \(-\Delta G^\circ\) (k.cals.mol\(^{-1}\)) | X    | Hammett \( \sigma \) | GB\(^{0}(b)\) (k.cals.mol\(^{-1}\)) | X    | Hammett \( \sigma \) | GB\(^{0}(b)\) (k.cals.mol\(^{-1}\)) |
|--------|------|---------------------|---------------------------------|------|---------------------|---------------------------------|------|---------------------|---------------------------------|
| 1      | 4-NH\(_2\) | -0.66               | 25.6                            | H    | 0.00                | 215.6                           | H    | 0.00                | 187.9                           |
| 2      | 4-MeO  | -0.27               | 15.7                            | 3-F  | 0.34                | 208.5                           | 4-F  | 0.06                | 182.9                           |
| 3      | 4-CHO  | 0.22                | 15.4                            | 3-Cl  | 0.37                 | 209.7                           | 4-Cl  | 0.23                | 183.8                           |
| 4      | 4-CN   | 0.66                | 11.4                            | 4-Cl  | 0.23                 | 212.2                           | 4-NO\(_2\) | 0.80              | 173.2                           |
| 5      | 4-OH   | -0.37               | 11.3                            | 4-Me  | -0.07                | 220.3                           | 4-MeO | -0.17               | 191.6                           |
| 6      | 4-NO\(_2\) | 0.80                | 8.9                             | 4-MeO | -0.27                | 223.6                           | 4-CF\(_3\) | 0.54              | 178.1                           |
| 7      | 4-Et   | -0.15               | 7.3                             | 4-CN  | 0.66                 | 203.8                           | 4-MeO | -0.27               | 197.1                           |
| 8      | 4-Me   | -0.17               | 6.3                             |                   |                     |                                 |                   |                     |                                 |
| 9      | H      | 0.00                | 0.0                             |                   |                     |                                 |                   |                     |                                 |
| 10     | 4-F    | 0.06                | -0.8                            |                   |                     |                                 |                   |                     |                                 |
| 11     | 4-Cl   | 0.23                | -1.0                            |                   |                     |                                 |                   |                     |                                 |

\(^{0(0)}}\)For the reaction (Yan K. Lau and Paul Kebarle, *J. Am. Chem. Soc.* 1976, 98, 23, 7452-7453, https://doi.org/10.1021/ja00439a072)

\(^{0(0)}}\)The GB values are from Nguyen-Nguyen Pham-Tran, Guy Bouchoux, David Delaere, and Minh Tho Nguyen, *J. Phys. Chem. A* 2005, 109, 2957-2963.
Figure 7 gives the Hammett $\rho$ for the proton transfer reaction of protonated benzene to substituted benzenes.

Figure 8 gives the Hammett $\rho$ for the gas phase basicities of pyridines.

Figure 9 gives the Hammett $\rho$ for the gas phase basicities of phosphorines.

Figure 10 gives the Hammett $\rho$ for the $\Delta G_{\text{solv}}$ versus Hammett $\sigma$ of free benzenes.

Figure 11 gives the Hammett $\rho$ for the $\Delta G_{\text{solv}}$ versus Hammett $\sigma$ of protonated benzenes.

Table 4. Solvation free energies ($\Delta G_{\text{solv}}$) of benzenes, pyridines, phosphorines (B) and their protonated species (BH$^+$)

| Sl. No. | X         | Benzene (XC$_5$H$_5$C) $\Delta G_{\text{solv}}$ (k.cal. mol$^{-1}$) | Pyridine (XC$_5$H$_4$N) $\Delta G_{\text{solv}}$ (k.cal. mol$^{-1}$) | Phosphorine (XC$_5$H$_4$P) $\Delta G_{\text{solv}}$ (k.cal. mol$^{-1}$) |
|---------|-----------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| 1       | 4-NH$_2$  | -0.66                                                         | H 0.00                                                         | H 0.00                                                         |
| 2       | 4-NHCH$_3$| -0.70                                                         | 3-F 0.34                                                        | 4-F 0.06                                                        |
| 3       | 4-NHC$_2$H$_5$| -0.61                                                       | 4-Cl 0.23                                                       | 4-Cl 0.23                                                       |
| 4       | 4-COCH$_3$| -0.50                                                         | 4-Me -0.07                                                      | 4-Me -0.17                                                      |
| 5       | 4-CN      | 0.66                                                          | 4-CN -4.10                                                      | 4-CN -3.44                                                      |
| 6       | 4-OH      | -0.37                                                         | 4-CN -6.45                                                      | 4-CN -3.34                                                      |
| 7       | 4-Et      | -0.15                                                         | 4-CN -3.34                                                      | 4-CN -3.34                                                      |
| 8       | 4-Me      | -0.17                                                         | 4-CN -3.34                                                      | 4-CN -3.34                                                      |
| 9       | H         | 0.00                                                          | -0.27                                                          | -0.27                                                          |
| 10      | 4-COOH    | 0.44                                                          | -0.87                                                          | -0.87                                                          |

Hammett $\rho$ for the free energy of solvation ($\Delta G_{\text{solv}}$) of free and protonated benzenes are -3.75 and -289 respectively.

\[^{a}\text{Are from http://ftp.aip.org/epaps/jcp_biochem_phys/E-JCPSA6-144-002616/supplmnt.pdf, G. Hou, X. Zhu, and Q. Cui, J. Chem. Theory Comput. 6, 2303 (2010), (b)The GB values are from Nguyen-Nguyen Pham-Tran, Guy Bouchoux, David Delaere, and Minh Tho Nguyen, J. Phys. Chem. A 2005, 109, 2957-2963, (c)Same value is reported by Takahashi H, Suzuoka D, Morita A, J Chem Theory Comput. 2015 Mar 10; 11(3):1181-94. doi: 10.1021/ct501133u.}\]

\[^{b}\text{Hammett $\sigma$ is calculated only from three substrates. not included in the correlation}\]

\[^{c}\text{Hammett $\rho$ for the free energy of solvation ($\Delta G_{\text{solv}}$) of free and protonated pyridines are 3.23 and -10.63 respectively not included in the correlation}\]

\[^{d}\text{Hammett $\rho$ for the free energy of solvation ($\Delta G_{\text{solv}}$) of free and protonated phosphorines are 2.35 and -9.78 respectively not included in the correlation}\]

Figure 10. Plot of $\Delta G_{\text{solv}}$ vs Hammett $\sigma$ for free benzenes

Figure 11. Plot of $\Delta G_{\text{solv}}$ vs Hammett $\sigma$ for protonated benzenes
Table 5. Hammett reaction constants ($\rho$) on different properties of benzenes (XC$_5$H$_5$C), pyridines (XC$_5$H$_4$N) and phosphorines (XC$_5$H$_4$P) and their protonated species

| On pK$_a$ (Data in Table 1) | On proton affinities (PA) (Data in Table 2) | On gas phase basicities (GB) (Data in Table 3) | On $\Delta G_{solv}$ (Data in Table 4) |
|---------------------------|---------------------------------|---------------------------------|---------------------------------|
| Arenium ions | Pyridinium ions | Phosphorenium ions | | | | | |
| 14.3 | 6.48 | 7.73 | |
| Figure 1 | Figure 2 | Figure 3 | |
| Benzenes | Pyridines | Phosphorines | |
| -30.5 | -21.8 | -20.1 | |
| Figure 4 | Figure 5 | Figure 6 | |
| Benzenes | Pyridines | Phosphorines | |
| -32.0 | -21.7 | -20.2 | |
| Figure 7 | Figure 8 | Figure 9 | |

-3.75 | -289 | 3.23 | -10.63 | 2.35 | -9.78
| Figure 10 | Figure 11 | Figure 12 | Figure 13 | Figure 14 | Figure 15 |

Calculated only from three points

Figure 12. Plot of $\Delta G_{solv}$ vs Hammett $\sigma$ of free pyridines

Figure 13. Plot of $\Delta G_{solv}$ vs Hammett $\sigma$ of protonated Pyridines

Figure 14. Plot of $\Delta G_{solv}$ versus Hammett $\sigma$ of free phosphorines

Figure 15. Plot of $\Delta G_{solv}$ versus Hammett $\sigma$ of protonated phosphorines
The trends in the Hammett $\rho$ values of the proton affinities (PA) and gas phase basicities (GB) of benzenes, pyridines and phosphorines are again in the same order of that observed for $pK_a$s (Table 5). At this point it is worth to discuss little about the proton affinities and gas phase basicities. Though they look same in brief but they differ thermodynamically. Proton affinity of a species $A^-$ is defined as the negative value of the enthalpy change ($\Delta H$) of the process shown in the following reaction.

$$A^- (g) + H^+ (g) \rightarrow AH (g)$$

And gas phase basicity is defined as the negative value of the corresponding Gibbs free energy change ($\Delta G$) of the same reaction [68,69]. It is known that $\Delta G = \Delta H - T\Delta S$. Therefore it is clear that both $\Delta G$ and $\Delta H$ differ by an amount of $T\Delta S$. And $\Delta H$ values are always higher by an amount of $T\Delta S$ than the values of $\Delta G$ (Table 2 and Table 3). From the trends of Hammett $\rho$ for PAs and GBs the same explanations offered hold good on Hammett $\rho$ for $pK_a$s given on page 5.

Effect of substituents on the trends in the Hammett $\rho$ values of $\Delta G_{solv}$ of the free and protonated benzenes, pyridines and phosphorines are rather complex. It is reported that there were two ways of approach of the addendum solvent molecule on to the benzene as shown below in A and B [70].

$$X = C \text{ or } N \text{ or } P$$

(B)

The solvolysis process is a result of a competition between $\pi$-electron interaction as shown in A and H-interaction of X-H bond ($X = C$ or $N$ or $P$) as shown in B with the approaching solvent molecule. From the negative Hammett $\rho$ value of -3.75 (Table 5, Figure 10) of the correlation of $\Delta G_{solv}$ values with Hammett $\sigma$ values in the present work for benzene clearly indicates that the interaction shown in A of scheme 1 may be predominant over the interaction shown in B. This is because the electron donating substituents are o,p-directing and they make the benzene molecule more electron rich at two ortho and at one para positions thus making the $\pi$-electron system of benzene more nucleophilic [71]. This makes easy for the positive part of addendum molecule to be attracted more by the benzene molecule. In the case of protonated benzenes high negative value of Hammett $\rho$ of -289 (Figure 11) is at present unexplainable. Probably one needs some more data of $\Delta G_{solv}$ for other substituents.

In the case of pyridines the Hammett $\rho$ value is positive and it is 3.23 (Table 5, Figure 12). Here the solvolysis process is a result of a competition between H-interaction of N-H bond and $\pi$-electron interaction with the approaching solvent molecule. In this process from the positive Hammett $\rho$ value of 3.23 suggests that the interaction of the type shown in B of scheme 1 is more favorable. This is because the electron withdrawing substituents at para position in pyridine moiety makes H of N-H bond more electrophilic hence the negative part of addendum molecule to be attracted more by the pyridine molecule.

In the case of protonated pyridines the whole process is just reversed as it can be seen from the negative Hammett $\rho$ value of -10.3 (Table 5, Figure 13).

And the same observations hold well for free and protonated phosphorines (Table 5, Figure 14 and Figure 15).

4. Conclusions

Trends in Hammett reaction constants ($\rho$) on $pK_a$s, proton affinities (PA), gas phase basicities (GB) and free energy of solvation ($\Delta G_{solv}$) of benzenes (XC₅H₄C), pyridines (XC₅H₄N) and phosphorines (XC₅H₄P) and their protonated species were discussed.

References

[1] Sanjeev Rachuru, and Jagannadham Vandanapu, Journal of Molecular Liquids, 2020, vol. 302, page 112496.
[2] R. Sanjeev, V. Jagannadham and R. Ravi, Chemical Methodologies, 2020, vol. 4 page 106-114
[3] Sanjeev, R. , David Geelan and Jagannadham Vandanapu, Journal of Molecular Liquids, 2020, vol. 298, page 112138.
[4] R. Sanjeev, R. Ravi and V. Jagannadham, National Academy of Science Letters (Allahabad, India), 2020, Vol. 43, page 5-8.
[5] R. Sanjeev, David Geelan and V. Jagannadham, Education Quimica (The Mexican Journal of Chemical Education), 2019, Vol. 30, page 83.
[6] Sanjeev Rachuru, V. Jagannadham and Sreedhar Pandiri, Oriental J. Chemistry, 2019, Vol. 35, page 461-465.
[7] R. Sanjeev and V. Jagannadham, Oriental Journal of Physical Sciences, Bhopal, India (2018) vol. 3, page 58-61.
[8] R. Sanjeev, D. A. Padmavathi and V. Jagannadham, World Journal of Chemical Education (Science & Educational Publishing, USA), (2018), Vol. 6, No. 1, page 78-81.
[9] R. Sanjeev, D. A. Padmavathi and V. Jagannadham, Oriental J. Chemistry, 2018, Volume 34, Number 1, page no. 526-531.
[10] Sanjeev, R. V. Jagannadham, Veda Vrath , R. V. E. M. Mamatha Bethapudi and Adam. A. Skelton, Oriental J. Chemistry, 2017, Volume 33, Number 5, page no.2673-2675.
[11] R. Sanjeev, R. Ravi and V. Jagannadham, Journal of Applicable Chemistry, 2017, vol. 6, page 665-667
[12] R. Sanjeev, V. Jagannadham, Adam A Skelton, Pandiri Sreedhar, V. E. M. Mamatha Bethapudi and R. Veda Vrath, Oriental J. Chemistry, 2017, Volume 33, Number 5, page no.2292-2296.
[13] R. Sanjeev and V. Jagannadham, Current Physical Chemistry published by Bentham Science publishers, USA 2017, vol. 7, page 1-6.
[14] R. Sanjeev, R. Ravi, V. Jagannadham and Adam A. Skelton, Australian Journal of Chemistry. Published online: 18 July 2016, in print 2017, vol. 70, page 90-100.
[15] Sanjeev Rachuru, V. Jagannadham, Adam A. Skelton, Journal of Molecular Liquids, 224 (2016) 43-46.
