

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

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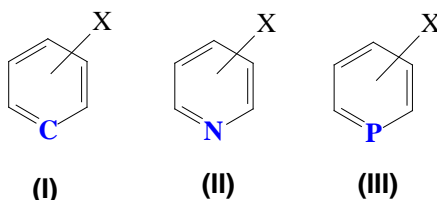
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Received August 15, 2020; Revised September 18, 2020; Accepted September 27, 2020

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 pK_a values of protonated pyridines and phosphorines. Trends in Hammett reaction constants (ρ) for all these processes were discussed.



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

Cite This Article: R. Sanjeev and V. Jagannadham, "Comparison of Substituent Effects in Benzenes (XC₅H₅C), Pyridines (XC₅H₄N) and Phosphorines (XC₅H₄P) and their Protonated Species." *World Journal of Chemical Education*, vol. 8, no. 4 (2020): 155-162. doi: 10.12691/wjce-8-4-3.

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 pK_a 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 pK_a, 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 pK_a 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 XC₆H₆⁺ ⇌ XC₆H₅ + 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 XC₆H₆⁺ ⇌ XC₆H₅ + 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 = m1⁽²⁻ⁱ⁾ [65] where m1 is an arbitrary constant "i" is the number of atoms between ionizable proton and the ring carbon.

Table 1. pK_a values of pyridinium and phosphorinium ions and Hammett ρ values for the three equilibria

$XC_6H_6^+ \rightleftharpoons XC_6H_5 + H^+$	$XC_5H_5N^+ \rightleftharpoons XC_5H_4N + H^+$				$XC_5H_5P^+ \rightleftharpoons XC_5H_4P + H^+$					
	Sl. No.	X	Hammett σ	$pK_a^{(a)}$		Sl. No.	X	Hammett σ	$pK_a^{(a)}$	
Hammett ρ for this equilibrium is 14.3 determined from the attenuation effect (Reference 26) Figure 1	1	H	0.00	5.21	Hammett ρ for this equilibrium is 6.48 Figure 2	1	H	0.00	-16.05	Hammett ρ for this equilibrium is 7.73 Figure 3
	2	3-F	0.34	2.93		2	4-F	0.06	-19.44	
	3	3-Cl	0.37	3.45		3	4-C	0.23	-18.60	
	4	4-Cl	0.23	4.52		4	4-NO ₂	0.78	-21.78	
	5	4-Me	-0.17	7.21		5	4-Me	-0.17	-15.53	
	6	4-MeO	-0.27	8.19		6	4-CF ₃	0.54	-21.22	
	7	4-CN	0.66	0.69		7	4-MeO	-0.27	-13.17	
	8	3-Me	0.07	5.70						
	9	4-NH ₂	-0.66	9.20						
	10	4-Et	-0.16	6.00						
	11	4-Me	-0.17	6.00						

^(a)The pK_a values are from Nguyen-Nguyen Pham-Tran, Guy Bouchoux, David Delaere, and Minh Tho Nguyen, *J. Phys. Chem. A* 2005, 109, 2957-2963.

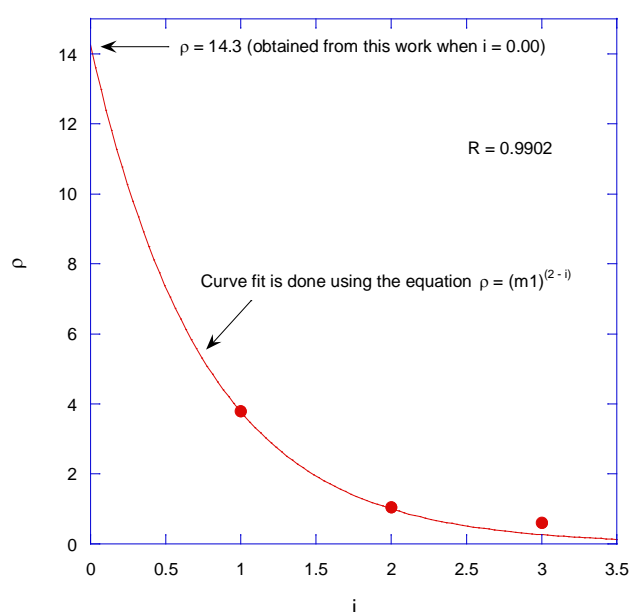


Figure 1. Plot of Hammett ρ versus i (the number of atoms between the ionizable proton and the ring carbon)

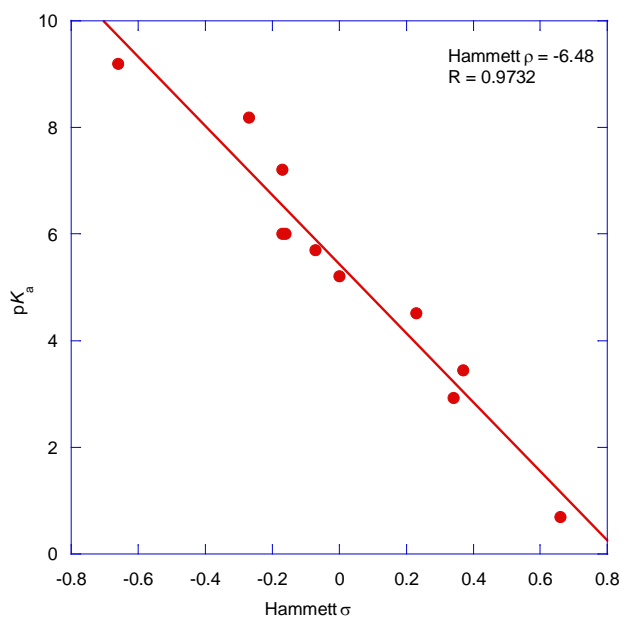


Figure 2. Plot of pK_a vs Hammett σ for pyridinium ions

Figure 2 shows the determination of the Hammett ρ for the dissociation equilibria of pyridinium ions $XC_5H_5N^+ \rightleftharpoons XC_5H_4N + H^+$ from the plot of pK_a versus Hammett σ .

Figure 3 shows the determination of the Hammett ρ for the dissociation equilibria of phosphorinium ions $XC_5H_5P^+ \rightleftharpoons XC_5H_4P + H^+$ from the plot of pK_a versus Hammett σ . The pK_a values of the equilibria $XC_5H_5N^+ \rightleftharpoons XC_5H_4N + H^+$ and $XC_5H_5P^+ \rightleftharpoons XC_5H_4P + H^+$ are from reference 66.

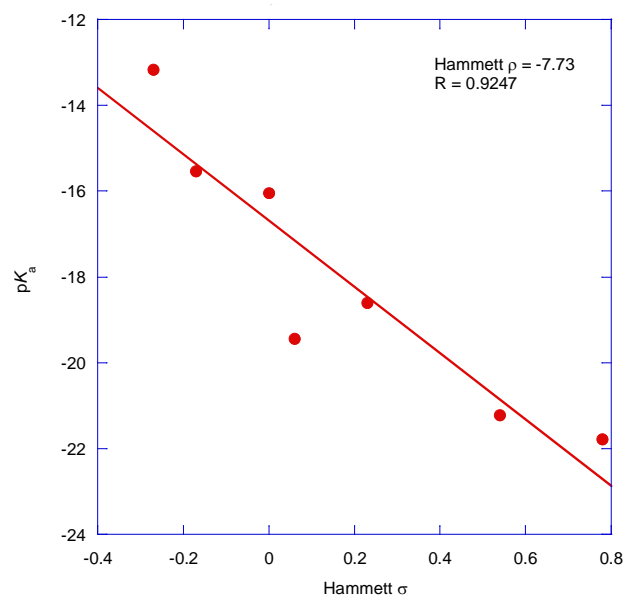


Figure 3. Plot of pK_a vs Hammett σ for phosphorinium ions

The negative Hammett ρ values for the equilibria $XC_5H_5N^+ \rightleftharpoons XC_5H_4N + H^+$ and $XC_5H_5P^+ \rightleftharpoons XC_5H_4P + H^+$ are from the plots of pK_a versus Hammett σ to be taken as positive for the plots of $\log K_a$ (since $-\log K_a = pK_a$) 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 $XC_6H_6^+ \rightleftharpoons XC_6H_5 + H^+$ and of the equilibria of $XC_5H_5N^+ \rightleftharpoons XC_5H_4N + H^+$ and $XC_5H_5P^+ \rightleftharpoons XC_5H_4P + H^+$. 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 the small difference of 1.25 units of Hammett ρ 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 reaction constants (ρ) 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 ρ for the proton affinities (PA) of benzenes from the plot of PAs versus Hammett σ .

Figure 5 shows the determination of the Hammett ρ for the proton affinities (PA) of pyridines from the plot of PAs versus Hammett σ .

Figure 6 shows the determination of the Hammett ρ for the proton affinities (PA) of phosphorines from the plot of PAs versus Hammett σ .

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

Sl. No.	benzene				pyridine			phosphorine		
	X	Hammett σ	PA (k.cals.mol ⁻¹)		X	Hammett σ	PA ^c (k.cals.mol ⁻¹)	X	Hammett σ	PA ^c (k.cals.mol ⁻¹)
			a	b						
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	-	3-Cl	0.37	217.5	4-Cl	0.23	191.5
4	4-CN	0.66	195	170	4-Cl	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	-	4-CN	0.66	211.5	4-MeO	-0.27	204.9
8	4-Me	-0.17	190	192	Hammett $\rho = -21.8$ Figure 5			Hammett $\rho = -20.1$ Figure 6		
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						

^aYan K. Lau and Paul Kebarle, *J. Am. Chem. Soc.* 1976, 98, 23, 7452-7453, <https://doi.org/10.1021/ja00439a072>.

^bfrom Pham-Cam Nam, and Minh Tho Nguyen, Asit K. Chandra, *J. Phys. Chem. A* 2006, 110, 4509-4515.

^cfrom reference 65.

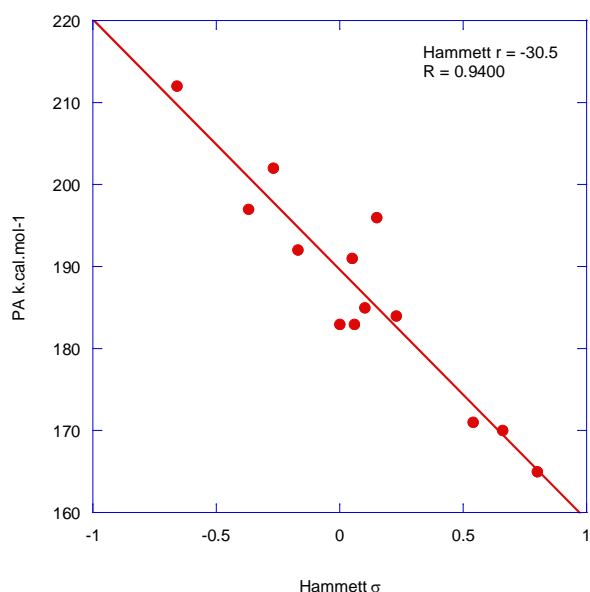


Figure 4. Plot of PAs vs Hammett σ for benzenes

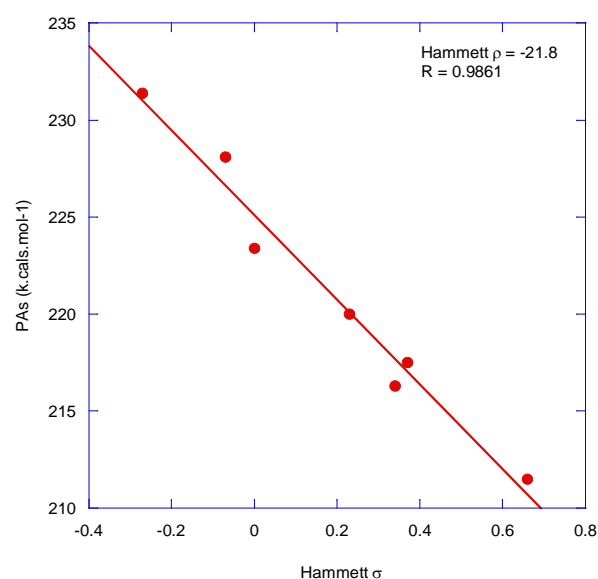


Figure 5. Plot of PAs versus Hammett σ for pyridines

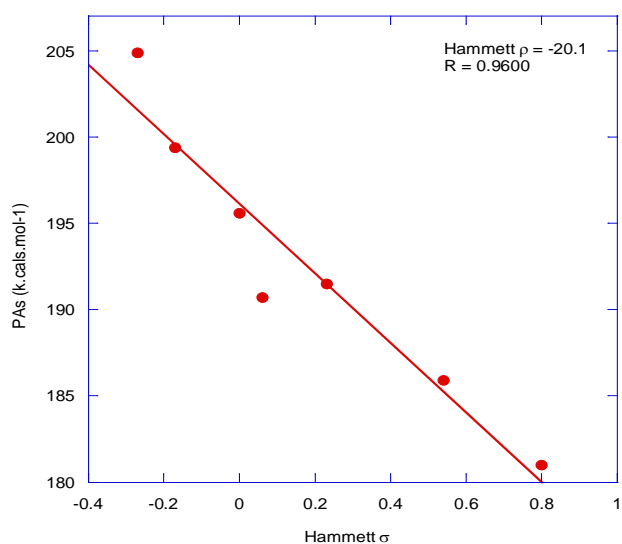


Figure 6. Plot of PAs versus Hammett σ for phosphorines

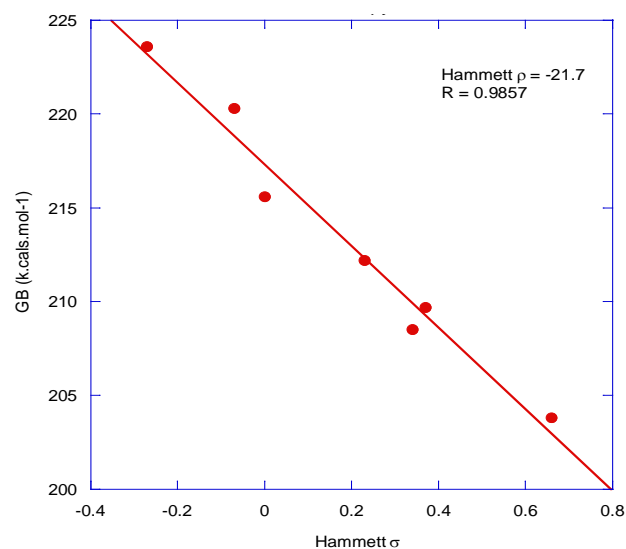


Figure 8. Plot of gas phase basicities (GB) vs Hammett σ for pyridines

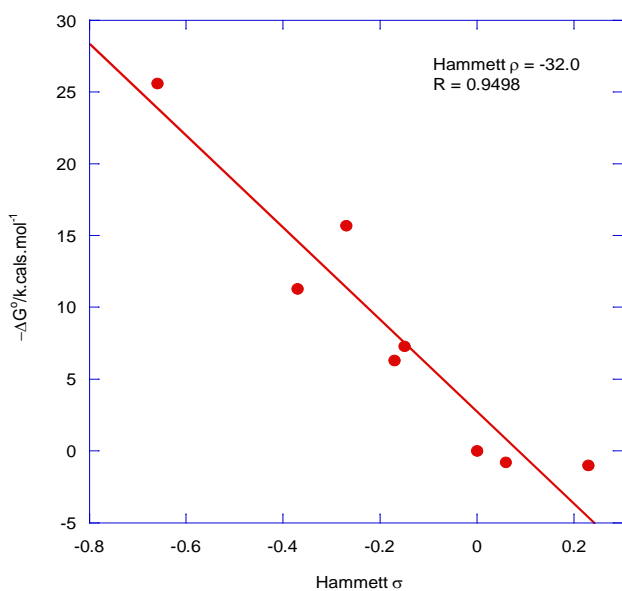


Figure 7. Plot of $-\Delta G^\circ$ vs Hammett σ for benzenes

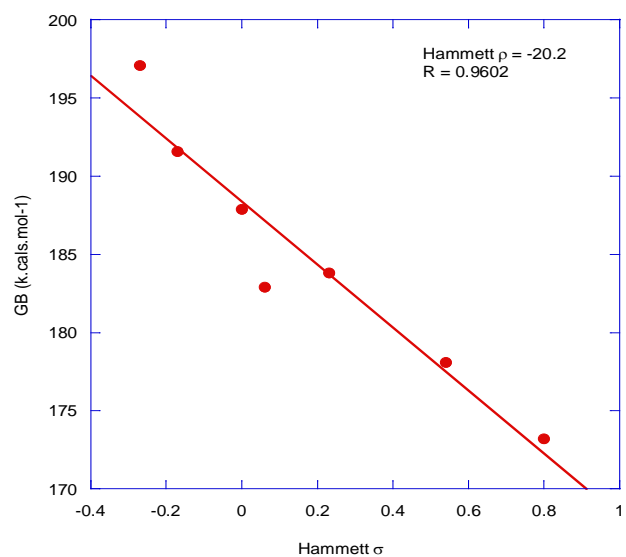
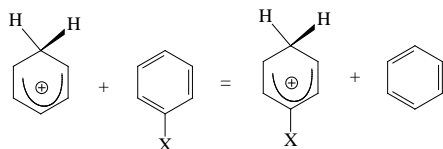


Figure 9. Plot of gas phase basicities (GB) vs Hammett σ for phosphorines

Table 3. $-\Delta G^\circ$ values of proton transfer to benzenes and gas phase basicities (GB) of pyridines and phosphorines

Sl. No.	benzene			pyridine			phosphorine		
	X	Hammett σ	$-\Delta G^{\circ(a)}$ (k.cals.mol ⁻¹)	X	Hammett σ	GB ^(b) (k.cals.mol ⁻¹)	X	Hammett σ	GB ^(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-Me	-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	Hammett ρ for this is -21.7 Figure 8			Hammett ρ for this is -20.2 Figure 9		
9	H	0.00	0.0						
10	4-F	0.06	-0.8						
11	4-Cl	0.23	-1.0						

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



^(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.

Figure 7 gives the Hammett ρ for the proton transfer reaction of protonated benzene to substituted benzenes.

Figure 8 gives the Hammett ρ for the gas phase basicities of pyridines.

Figure 9 gives the Hammett ρ for the gas phase basicities of phosphorines.

Figure 10 gives the Hammett ρ for the ΔG_{solv} versus Hammett σ of free benzenes.

Figure 11 gives the Hammett ρ for the ΔG_{solv} versus

Hammett σ of protonated benzenes.

Figure 12 gives the Hammett ρ for the ΔG_{solv} versus Hammett σ of free pyridines.

Figure 13 gives the Hammett ρ for the ΔG_{solv} versus Hammett σ of protonated pyridines.

Figure 14 gives the Hammett ρ for the ΔG_{solv} versus Hammett σ of free phosphorines.

Figure 15 gives the Hammett ρ for the ΔG_{solv} versus Hammett σ of protonated phosphorines.

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

Sl. No.	Benzene ($\text{XC}_5\text{H}_5\text{C}$)				Pyridine ($\text{XC}_5\text{H}_4\text{N}$)				Phosphorine ($\text{XC}_5\text{H}_4\text{P}$)			
	X	Hammett σ	ΔG_{solv} (k.cal. mol ⁻¹)		X	Hammett σ	$\Delta G_{\text{solv}}^{(b)}$ (k.cal. mol ⁻¹)		X	Hammett σ	$\Delta G_{\text{solv}}^{(b)}$ (k.cal. mol ⁻¹)	
			B ^(a)	BH ^{+(a)}			B	BH ⁺			B	BH ⁺
1	4-NH ₂ (4-NH ₃ ⁺)	-0.66 1.13 is used	-5.49	-70.0	H	0.00	-4.85	-55.63	H	0.00	-2.77	-52.31
	4-N(Et) ₂	-0.72	-	-52.0	3-F	0.34	-4.34	-59.10	4-F	0.06	-2.01	-51.83
	4-NHCH ₃	-0.70	-	-61.0	3-Cl	0.37	-3.70	-57.96	4-Cl	0.23	-1.77	-51.92
	4-NHC ₂ H ₅	-0.61	-	-60.0*	4-Cl	0.23	-3.37	-56.63	4-NO ₂	0.80	-3.85*	-60.21
2	4-COCH ₃	0.50	-	-63.0*	4-Me	-0.07	-4.54	-53.35	4-Me	-0.17	-2.56	-49.03
3	4-MeO	-0.27 0.12 is used	-2.45	Hammett ρ is calculated only from three substrates. *not included in the correlation	4-MeO	-0.27	-6.12	-52.98	4-CF ₃	0.54	-1.31	-53.54
4	4-CN	0.66	-4.10		4-CN	0.66	-6.45*	-62.89	4-MeO	-0.27	-3.34	-47.53
5	4-OH	-0.37 0.12 is used	-6.62		Hammett ρ for the free energy of solvation (ΔG_{solv}) of free and protonated pyridines are 3.23 and -10.63 respectively *is not included in the correlation Figure 12 and 13				Hammett ρ for the free energy of solvation (ΔG_{solv}) of free and protonated phosphorines are 2.35 and -9.78 respectively *is not included in the correlation Figure 14 and 15			
6	4-NO ₂	0.80	-4.12									
7	4-Et	-0.15	-0.80									
8	4-Me	-0.17	-0.89									
9	H	0.00	-0.87 ^(c)									
10	4-COOMe	0.44	-3.10									
Hammett ρ for the free energy of solvation (ΔG_{solv}) of free benzenes is -3.75 and protonated benzenes is -289 Figure 10 and 11 respectively												

^(a)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/ct5011133u.

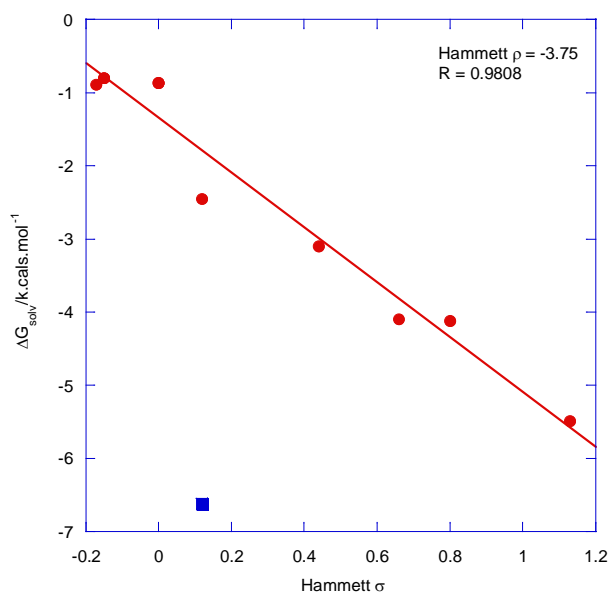


Figure 10. Plot of ΔG_{solv} vs Hammett σ for free benzenes

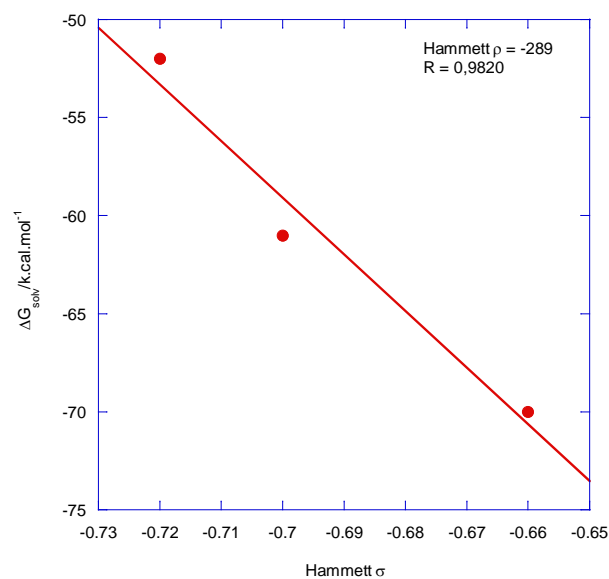
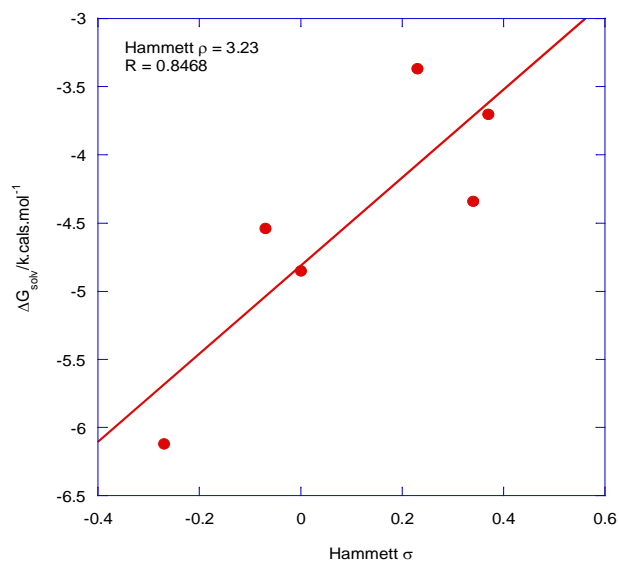
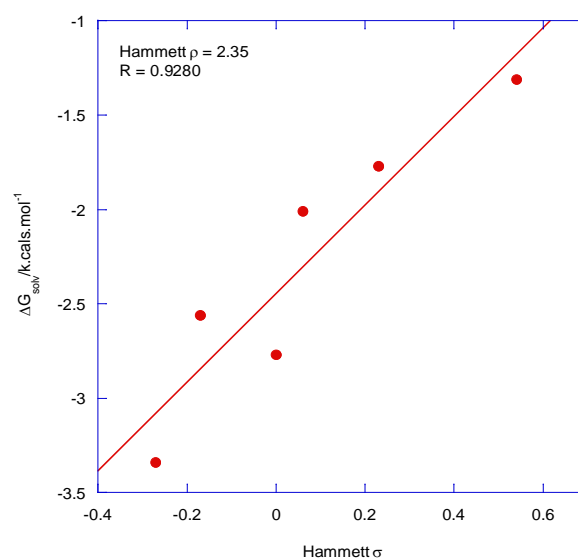
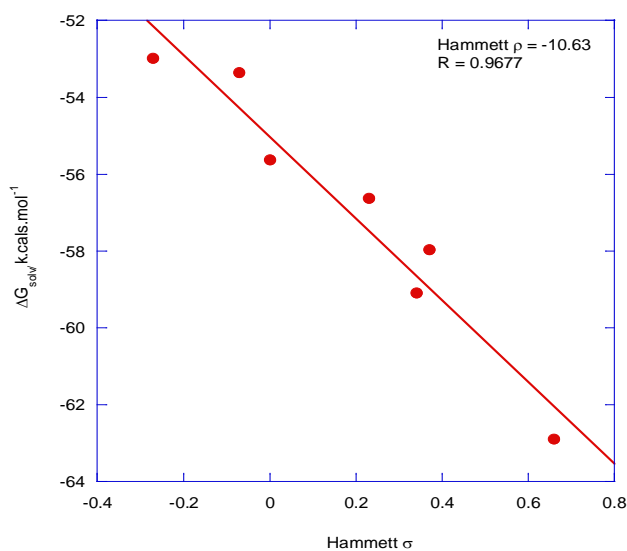
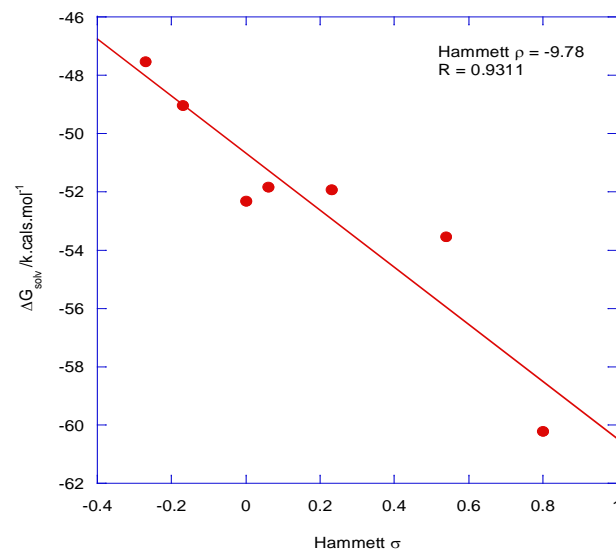
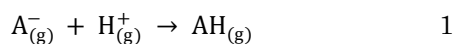


Figure 11. Plot of ΔG_{solv} vs Hammett σ for protonated benzenes

Figure 12. Plot of ΔG_{solv} vs Hammett σ of free pyridinesFigure 14. Plot of ΔG_{solv} versus Hammett σ of free phosphorinesFigure 13. Plot of ΔG_{solv} vs Hammett σ of protonated PyridinesFigure 15. Plot of ΔG_{solv} versus Hammett σ of protonated phosphorinesTable 5. Hammett reaction constants (ρ) on different properties of benzenes ($\text{XC}_6\text{H}_5\text{C}$), pyridines ($\text{XC}_5\text{H}_4\text{N}$) and phosphorines ($\text{XC}_5\text{H}_4\text{P}$) and their protonated species

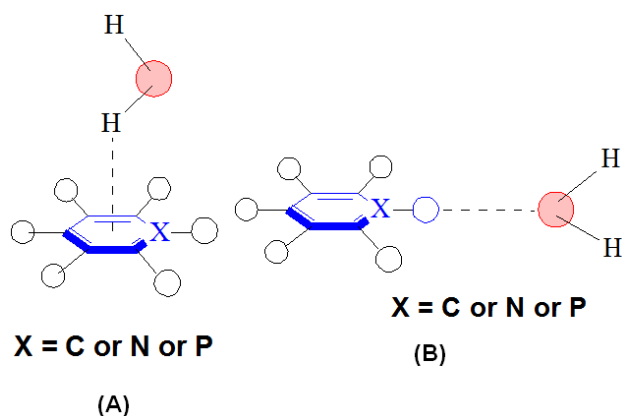
On pK_a (Data in Table 1)					
Arenium ions		Pyridinium ions		Phosphonium ions	
14.3		6.48		7.73	
Figure 1		Figure 2		Figure 3	
On proton affinities (PA) (Data in Table 2)					
Benzenes		Pyridines		Phosphorines	
-30.5		-21.8		-20.1	
Figure 4		Figure 5		Figure 6	
On gas phase basicities (GB) (Data in Table 3)					
Benzenes		Pyridines		Phosphorines	
-32.0		-21.7		-20.2	
Figure 7		Figure 8		Figure 9	
On ΔG_{solv} (Data in Table 4)					
Benzenes		Pyridines		Phosphorines	
B	BH^+	B (free base)	BH^+ (protonated base)	B (free base)	BH^+ (protonated base)
-3.75	-289	3.23	-10.63	2.35	-9.78
Figure 10	Figure 11 Calculated only from three points	Figure 12	Figure 13	Figure 14	Figure 15

The trends in the Hammett ρ 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 (ΔH) of the process shown in the following reaction.



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

Effect of substituents on the trends in the Hammett ρ values of ΔG_{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].



Scheme 1.

The solvation process is a result of a competition between π -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 ρ value of -3.75 (Table 5, Figure 10) of the correlation of ΔG_{solV} values with Hammett σ 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 π -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 ρ of -289 (Figure 11) is at present unexplainable. Probably one needs some more data of ΔG_{solV} for other substituents.

In the case of pyridines the Hammett ρ value is positive and it is 3.23 (Table 5, Figure 12). Here the solvation process is a result of a competition between H-interaction of N-H bond and π -electron interaction with the approaching solvent molecule. In this process from the positive Hammett ρ 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 ρ 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 (ρ) on pK_a s, proton affinities (PA), gas phase basicities (GB) and free energy of solvation (ΔG_{solV}) of benzenes (XC_5H_5C), pyridines (XC_5H_4N) and phosphorines (XC_5H_4P) and their protonated species were discussed.

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