



Tetrahedral Nature Determines the Stability of Reactive Intermediates: A Chemical Education Perspective

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ABSTRACT

Hammett equation is applied and the magnitude of substituent effect in terms of Hammett ρ has been estimated for the deprotonation equilibriums of highly unstable arenium ions (*Wheland intermediates*) $\text{XC}_6\text{H}_6^+ \rightleftharpoons \text{XC}_6\text{H}_5 + \text{H}^+$ based on the attenuation effect of methylene group on the dissociation equilibriums of anilinium ions, benzyl ammonium ions and 2-phenylethyl ammonium ions. The Hammett ρ was found to be 14.3. The Hammett ρ for the deprotonation equilibriums of pyridinium ions $\text{XC}_5\text{H}_4\text{NH}^+ \rightleftharpoons \text{XC}_5\text{H}_4\text{N} + \text{H}^+$ was estimated from the plot of $\log K_a$ vs Hammett σ , this value is 5.90. The magnitude of substituent effect in terms of Taft ρ^* has been estimated for the deprotonation equilibriums of methanium ions $\text{RCH}_4^+ \rightleftharpoons \text{RCH}_3 + \text{H}^+$ based on the attenuation effect of methylene group on the dissociation equilibriums of aliphatic amines and was found to be 6.9. The Taft ρ^* for the deprotonation equilibriums of alkyl ammonium ions $\text{RNH}_3^+ \rightleftharpoons \text{RNH}_2 + \text{H}^+$ was estimated from the plot of $\log K_a$ vs Taft σ^* , this value is 3.28. The large differences in the Hammett ρ of 8 units when carbon is replaced with nitrogen as heteroatom in the six-member aromatic ring and 3.6 units of Taft ρ^* when carbon is replaced with nitrogen in aliphatic derivatives respectively is explained.

INTRODUCTION

The frequent over viewing and dealing with Hammett and Taft equations is a continuous well documented observation from our laboratory¹⁻¹⁶. In all these studies application of Hammett and Taft equations is dealt in detail and even to physical properties like dipole moments, surface tensions and melting points of several organic compounds.

But application of Hammett and Taft equations to very unstable intermediates is a challenging task. Application of Hammett and Taft equations to arenium ions¹⁰ (*Wheland intermediates*, XC_6H_6^+) and methanium ions¹⁵ (super acids, RCH_4^+) is itself novel. In the present work we tried to explain why the deprotonation equilibriums of arenium ions (*Wheland intermediates*, XC_6H_6^+) and methanium ions (super acids, RCH_4^+) are more susceptible to substituent



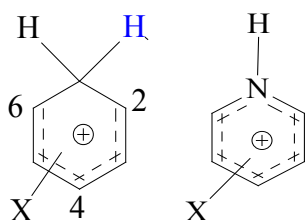
effects than the deprotonation equilibria of the corresponding nitrogen analogues, the pyridinium ions ($\text{XC}_5\text{H}_4\text{NH}^+$) and the alkyl ammonium ions (RNH_3^+) respectively?

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.

DISCUSSION

Arenium ions are formed as unstable intermediates by the attack of a positive ion or a dipole on the benzene¹⁷. The known simplest arenium ion is the benzenonium ion 1 (scheme 1) with $\text{X} = \text{H}$ prepared in $\text{HF-SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$ at -134°C by Olah group¹⁸.



Scheme 1

In fact not all chemical species are readily open to experimental characterization. Determination of any physical property like Hammett reaction constant (ρ), from the plot of pK_a ($-\log K_a$) versus Hammett σ of these benzenonium ions is extremely difficult. It may be possible by time resolved optical methods which is very expensive and time consuming. We have achieved a simple and lucid protocol and is presented in our earlier¹⁰ article for the evaluation of the Hammett reaction constant (ρ) of the deprotonation process of these benzenonium (arenium) ions $\text{XC}_6\text{H}_6^+ \rightleftharpoons \text{XC}_6\text{H}_5 + \text{H}^+$ based on the attenuation effect of methylene group on the dissociation equilibria of anilinium ions, benzyl ammonium ions and 2-phenylethyl ammonium ions. Using the pK_a values of anilinium ions, benzyl ammonium ions and 2-phenylethyl ammonium ions the Hammett ρ values were first estimated for the three equilibria from the plot of $\log K_a$ versus Hammett σ . Then using the equation $\rho = m_1^{(2-i)}$ from Andrew Williams treatment¹⁹, the Hammett ρ is determined

for the deprotonation process of arenium ions $\text{XC}_6\text{H}_6^+ \rightleftharpoons \text{XC}_6\text{H}_5 + \text{H}^+$ for $i = 0$, from the interpolation of the locus of the plot of Hammett ρ versus 'i' where 'i', the number atoms (number of $-\text{CH}_2-$ groups) between the ionizable proton and the ring carbon atom (Fig. 1) and it was found to be 14.3.

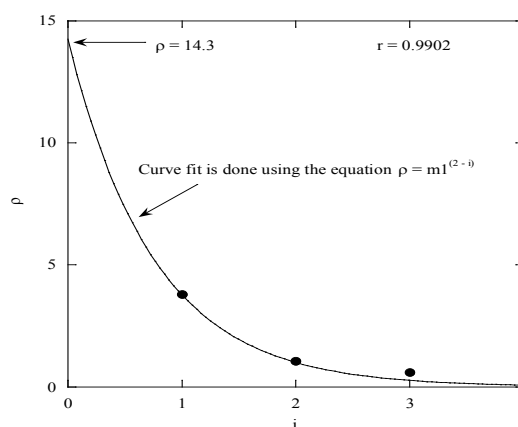
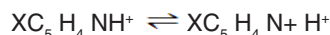


Fig. 1. Plot of Hammett ρ versus i (the number of atoms between the ionizable proton and the ring carbon)

The Hammett ρ for the deprotonation equilibria of pyridinium ions



was estimated from the plot of $\log K_a$ vs Hammett σ , this value is found to be 5.90, Figure 2)

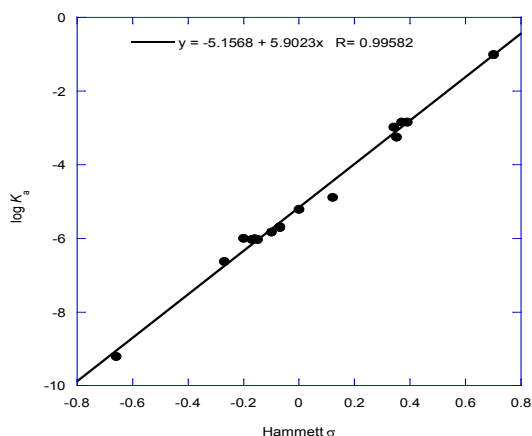


Fig. 2. Plot of $\log K_a$ vs Hammett sigma of pyridines

The magnitude of substituent effect in terms of Taft ρ^* has been estimated for the deprotonation equilibria of methanium ions $\text{RCH}_4^+ \rightleftharpoons \text{RCH}_3 + \text{H}^+$ again using William's treatment¹⁹ based on the attenuation effect of methylene group on the

dissociation equilibria of aliphatic amines and was found to be 6.9 (Figure 3).

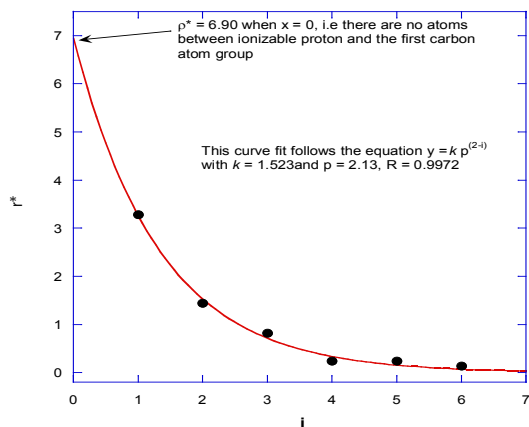


Fig. 3. Plot of r^* versus "i" the number of atoms between ionizable proton and the first carbon atom of the alkyl substituent

The Taft ρ^* for the deprotonation equilibria of alkyl ammonium ions $\text{RNH}_3^+ \rightleftharpoons \text{RNH}_2 + \text{H}^+$ was estimated from the plot of $\log K_a$ vs Taft σ^* and was found to be 3.28 (Figure 4).

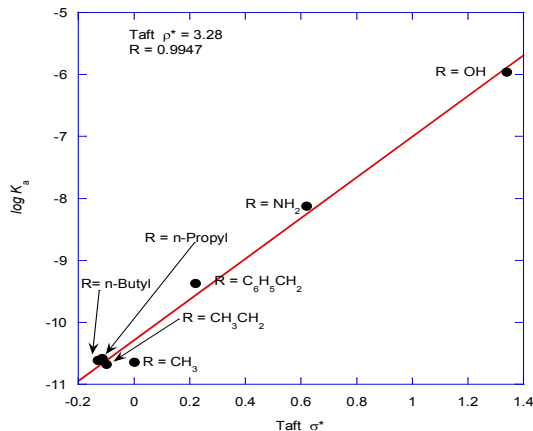
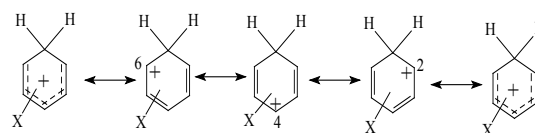


Fig. 4. Plot of $\log K$ versus Taft σ^* values of alkyl ammonium ions (RNH_3^+) with one atom between ionizable proton and the first carbon atom of the substituent

The large decrease in the Hammett ρ of 8 units when carbon is replaced with nitrogen as hetero atom in the six-member aromatic ring and 3.6 units of Taft ρ^* when carbon is replaced with nitrogen in aliphatic derivatives respectively is explained as follows:

The formation and deprotonation of 1 is well discussed¹⁷. The discernible difference between the formation of benzenonium ion 1 and pyridinium

ion 2 is the loss of aromaticity of benzene and yet still retention of aromaticity of pyridine respectively. The octet of one of the three carbons 2, 4 and 6 in benzenonium ion 1 (scheme 2) in which to the carbon 1 the proton is attached is incomplete. At any given point of time one of the three carbons carries the positive charge and the octet is incomplete. Pyridinium cations 2 are aromatic ions, as determined by Hückel's rule²⁰. It is isoelectronic to benzene. The octet of nitrogen in pyridinium ion is still intact. Therefore in terms of stability, pyridinium ion 2 is more stable than the benzenonium ion 1.



Scheme 2

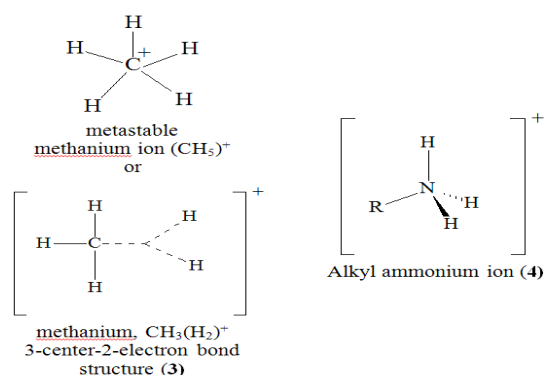
Another important point to note is the difference in the hydrophilic character of carbon and nitrogen. It is a well recognized fact that ammonia (NH_3) is more hydrophilic than methane (CH_4)²¹. An example of this is the presence of nitrogen in a sp^2 carbon framework increases the hydrophilic character of carbon nano tubes because N-doped carbon nano tubes are more polar than neat carbon nano tubes^{22, 23}. The higher the polarity the more favorable will be the interaction of a substance with hydrophilic solvents like water. Pyridine is nothing but a molecule with nitrogen in a sp^2 carbon framework. Therefore in terms of stability and hydrophilicity, among the transition states during the formation of arenium ions and pyridinium ions, the transition states of pyridinium ions are more hydrophilic, hence solvated by water more efficiently and are therefore more stable. In effect, hydrogen bonding to the nitrogen in pyridinium ion partially quenches the unit positive charge on nitrogen. Consequently, the Hammett ρ value is less than that for arenium ions deprotonation equilibrium. The nitrogen in pyridium ion is tertiary and it is known that the tertiary nitrogen ions are more effectively hydrated/solvated than the bare nitrogen in tertiary amines^{24, 25, 26}. Invoking reactivity-selectivity principle²⁷ the more stable species is less susceptible to any other effect exerted on it. Therefore the substituent effects on the deprotonation equilibria of pyridinium ions are less than those of the arenium ions. This is reflected on the Hammett ρ values of both the deprotonation equilibria. The Hammett ρ value of 14.3 of arenium ion deprotonation equilibria is more than the value of 5.9 of pyridinium ions.

Similar is the situation with methanium ions and alkylammonium ions. Again the perceptible difference between methanium ion 3 and alkylammonium ion 4 is the loss of tetrahedral nature of methane on protonation and yet the intactness of the tetrahedral nature of alkyl amine even after formation of alkyl ammonium ion (scheme 3).

Invoking all the arguments offered for the arenium and pyridinium ions above, it can be inferred that the Taft ρ^* value of 6.9 for the deprotonation equilibriums of methanium ions is greater than that of 3.28 for the alkylammonium ions.

CONCLUSION

The deprotonation equilibriums of arenium ions (Wheland intermediates, XC_6H_6^+) and methanium ions (super acids, RCH_4^+) are more susceptible to substituent effects than the deprotonation equilibriums of pyridinium ions ($\text{XC}_5\text{H}_4\text{NH}^+$) and alkyl ammonium ions (RNH_3^+) respectively. This is explained on the basis of the retention of the tetrahedral nature of



Scheme is inserted

Scheme 3

the alkyl amines even after the formation of the respective alkyl ammonium ions on protonation. But on protonation the tetrahedral nature of methane is lost after formation of methanium ion.

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