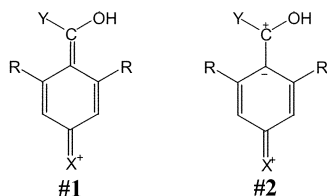


Notes

Transmission of Substituent Effects in the Protonation of Substituted 2-Furaldehydes in Sulfuric Acids

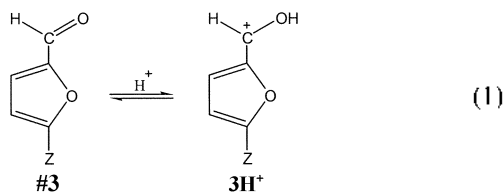
Ikchoon Lee,^{*} Tae Seop Uhm,[§] Zoon Ha Ryu,[†] In Sun Koo,[‡] and Jong Pal Lee^{§,*}*Department of Chemistry, Inha University, Incheon 402-751, Korea**[†]Department of Chemistry, Donggeui University, Pusan 614-714, Korea**[‡]Department of Chemical Education, Gyeongsang National University, Chinju 660-701, Korea**[§]Department of Chemistry, Dong-A University, Pusan 604-714, Korea**Received February 21, 2002***Keywords :** Excess acidity, Protonation, 5-Substituted-2-furaldehydes.

The transmission of substituent effects through aromatic and heteroaromatic ring has been the subject of extensive studies.¹ Experimentally, carbonyl group is one of the most commonly used and versatile probe for studying the substituent ring probe interactions.^{1e,2} The protonation equilibria of a number of carbonyl compounds such as aromatic acids,^{1f} ketones^{1b,g,3} aldehydes,¹ⁱ amides^{1k,4} and esters^{1b} have been reported in concentrated solutions of mineral acid.



An interesting aspect of the results of these studies is that the resonance effect of an electron donor ($\sigma_X < 0$) has to be regarded as a blend of normal conjugation (#1) and Π -polarization (#2). The Π -polarization mechanism (#2) has been found to apply in the hindered ($R = \text{CH}_3$) as well as unhindered ($R = \text{H}$) series of carbonyl compounds.^{1f,3}

In this work, the protonation equilibria of 2-furaldehydes (#3), have been studied in aqueous sulfuric acid solution at 298 K, eq. (1) where $Z = \text{CH}_3, \text{H}, \text{Br}$ and NO_2 . The purpose



of this work is to examine whether the Π -polarization mechanism also applies to the 5-membered heteroaromatic ring systems, and if so, what causes to favor the Π -polarization (#2) rather than direct conjugation (#1)?

Experimental Section

Materials. The substrates, 2-furaldehydes were Aldrich special grade reagents. The water was degassed by bubbling through nitrogen gas and the sulfuric acid solution were titrated by 0.1 N NaOH to exact concentrations.

pK_{BH+} Measurements. Ionization ratios, $I = C_{\text{BH}^+}/C_{\text{B}}$ where C_{BH^+} and C_{B} are molar concentrations of conjugate acid and base, were determined spectrophotometrically by eq. (2) where the absorbance D was recorded immediately

$$I = C_{\text{BH}^+}/C_{\text{B}} = (D - D_{\text{B}})/(D_{\text{BH}^+} - D) \quad (2)$$

after addition of the substrate into aqueous sulfuric acids of given concentration and D_{B} is the absorbance of the unprotonated substrate and D_{BH^+} that of its conjugate acid. The pK_{BH+} values for each compound were obtained by means of the excess acidity method,^{1f,3,4} eq. (3) where X is the excess acidity (EA).

$$\log I - \log C_{\text{H}^+} = m^*X + \text{pK}_{\text{BH}^+} \quad (3)$$

The C_{BH^+} and X values used in eq. (3) were calculated by interpolation of literature data.^{5,6} The slope, m^* , reflects primarily the susceptibility of the protonated substrate to

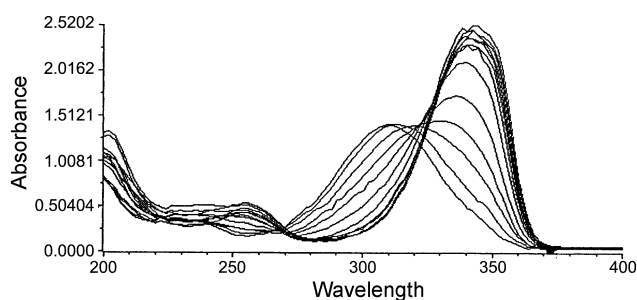


Figure 1. Absorption spectra for protonation of 5-bromo-2-furaldehyde in the range of 70 w/w%-94 w/w% aqueous sulfuric acid solution.

Table 1. Maximum absorption wavelengths for base B and the corresponding protonated form BH⁺ of 5-substituted-2-furaldehydes (5-Z-FA)

Z	5-Z-FA	
	B	BH ⁺
	λ_{max}	λ_{max}
CH ₃	294	326
H	278	308
Br	292	340
NO ₂	310	320

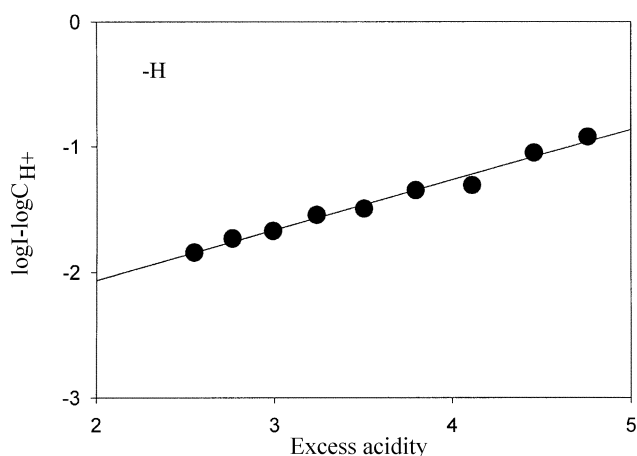
Table 2. Values of excess acidity function and ionization ratio of 2-furaldehyde in 52.5 w/w%-72.0 w/w% aqueous sulfuric acid at 25 °C

w/w% acid	logC ₁₁	X	D ₃₀₈	logI	logI/C ₁₁
52.5	0.970	2.548	0.419	-0.873	-1.844
55.0	0.992	2.763	0.501	-0.741	-1.733
57.5	1.014	2.992	0.563	-0.657	-1.671
60.0	1.033	3.238	0.689	-0.512	-1.545
62.5	1.052	3.505	0.758	-0.443	-1.495
65.0	1.069	3.795	0.942	-0.279	-1.348
67.5	1.084	4.112	1.009	-0.224	-1.308
70.0	1.097	4.459	1.364	0.049	-1.048
72.0	1.108	4.759	1.544	0.187	-0.921

stabilization by solvation (especially through hydrogen bonding). A typical absorption spectra in series of aqueous sulfuric acid solutions are shown in Figure 1, and the maximum absorption wavelengths (λ_{max}) used in the determination of ionization ratio, I, are summarized in Table 1.

Results and Discussion

The raw data for determination of the pK_{BH⁺} value by eq. (3) are shown for Z = H in Table 2 and the plot of logI -

**Figure 2.** Plot of (logI - logC₁₁) vs. excess acidity for 2-furaldehyde in aqueous sulfuric acid at 25 °C.**Table 3.** Acid dissociation constants, pK_{BH⁺} and m* values for 5-Z-2-furaldehyde (5-Z-FA) in aqueous sulfuric acid at 25 °C

Z	5-Z-FA		
	pK _{BH⁺}	m*	Δ pK _{BH⁺}
CH ₃	-2.50	0.39	-0.37
H	-2.87	0.40	0.00
Br	-3.15	0.44	0.28
NO ₂	-5.75	0.66	2.88

* Δ pK_{BH⁺} = (pK_{BH⁺})_H - (pK_{BH⁺})_Z

logC₁₁ versus X is presented in Figure 2.

All the plots exhibited good linearities and the pK_{BH⁺} and m* values determined are collected in Table 3. Reference to Table 3 reveals that the magnitude of m* values (0.39-0.66) is relatively small and are similar to those for the protonation of benzamide (0.57)^{1k}, acetamide (0.55)^{1k} and benzoic acids (0.49-0.56).^{1f} These smaller m* values are in contrast to significantly higher values for the protonation of primary anilines (m* = 1.00)^{5,6} and ketones (2-acetylthiophenes, m* = 0.85; phenylthiophen-2-yl methanones, m* = 0.97).^{1g} The small m* values are believed to provide primary evidence of strong hydrogen bonding of the protonated forms (BH⁺) in H₂O.¹

Our plots of the basicity (pK_{BH⁺}) against σ_p^+ and σ_p^- showed negative slopes ($\rho^+ = -3.12 \pm 0.57$, $\rho^- = -3.47 \pm 0.61$) with slightly better correlation for the latter (r = 0.968 and 0.971, respectively). Although the difference in the correlation coefficients is small, the fact that the σ_p^- plot did not give a better correlation indicates that through-conjugation mode (#1) is not predominant.¹

There is a fairly good linearity (r = 0.971) in the plot of m* versus σ_p with a positive slope (0.30 ± 0.05). This is an indication that the solvation of the BH⁺ forms is closely related to the substituent effects. The dependence of pK_{BH⁺} on m* is given by eq. (4).

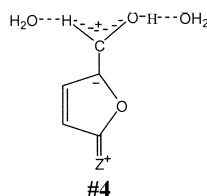
$$\text{pK}_{\text{BH}^+} = -11.63 \pm 0.63 m^* + 1.93 \pm 0.29 \quad (r = 0.997) \quad (4)$$

It is important that the slope (in eq. 4) is negative. This is qualitatively opposite to that commonly found,⁶ where a stronger solvation (with lower m* values) is generally required when BH⁺ is less stabilized by the substituent electronic effects. Thus if the mode of substituent effect transmission were the through-conjugation type (#1), an electron donor ($\sigma_p < 0$) should be stabilized by the through-conjugation (#1) and the m* value should be higher.^{3,4} The opposite trends, i.e., the smaller m* value for an electron donor, found in the present work (Table 3) is therefore an indication that the through-conjugation mode is not operative.

We therefore conclude that the substituent effects are transmitted by the Π -polarization mode (#2) in the protonated forms of 2-furaldehydes (3H⁺) based on (i) the relatively strong solvation BH⁺ with lower m* values, (ii) no better correlation with σ_p^- and (iii) the negative slope in eq. (4).

We think that strong solvation of 3H⁺ with an electron

donor ($Z = \text{CH}$) is provided by the relatively low delocalizability of the oxygen atom in the hetero ring toward the carbonyl group. Theoretical analyses⁷ at the MP2/6-31G^{*} level⁸ indicated that the through-conjugation in the 3H^+ is lower than the corresponding mode in the protonated benzaldehyde. Thus solvation by H_2O can occur at two sites, **#4**, which is similar to that suggested for the hydration of benzoic acids.^{1f}



The strong solvation of the BH^+ forms with donor (σ_20) is only possible in the Π -polarization mode leading to the low m^* values and to the low possibility of the through-conjugation mode. This is supported by the similar low m^* values obtained for the protonation of hindered ($\text{R} = \text{CH}$ in **#1** and **#2**) as well as unhindered ($\text{R} = \text{H}$) benzoic acids ($\text{Y} = \text{OH}$),^{1f} acetophenones ($\text{Y} = \text{CH}_3$),³ methyl benzoates ($\text{Y} = \text{OCH}_3$)^{1b,c} and benzamides ($\text{Y} = \text{NH}$) with electron donor substituents. In all of these cases, Π -polarization is considered to represent the main resonance interaction mode between para-substituents and the carbonyl moiety.

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