Notes

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

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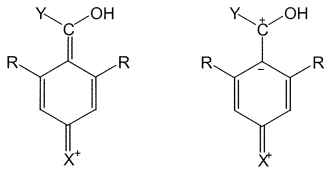
Received February 21, 2002

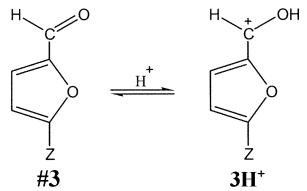
Keywords : Excess acidity, Protonation, 5-Substituted-2-furaldehydes.

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.[1g,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 = CH_3) as well as unhindered (R = 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 = CH_3, H, Br and NO_2. The purpose



(1)

of this work is to examine whether the Π-polarization mechanism also applies to the 5-memberd 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, $I = C_{BH^+}/C_B$ where C_{BH^+} and C_B are molar concentrations of conjugate acid and base, were determined spectrophotometerically by eq. (2) where the absorbance D was recorded immediately

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

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).

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

The C_{H^+} 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

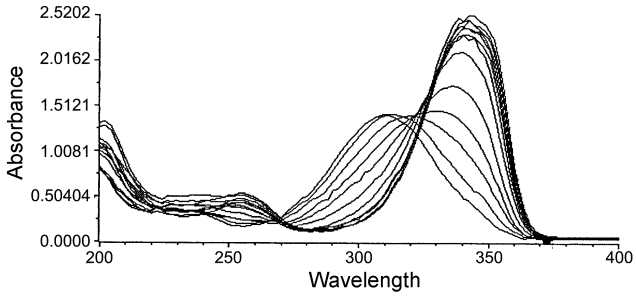


Figure 1. Absortion spectra for protonation of 5-bormo-2-furaldehyde in the range of 70 w/w%-94 w/w% aqueous sulfuric acid solution.

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	$logC_{H+}$	X	D_{308}	logI	$logI/C_{H+}$
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 – $logC_{H+}$ versus X is presented in Figure 2.

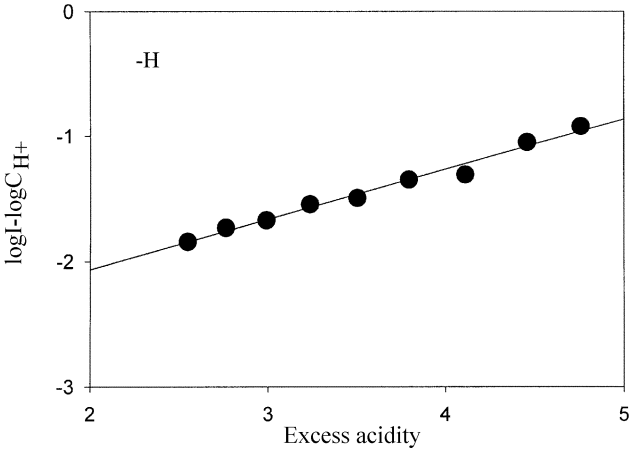


Figure 2. Plot of ($logI–logC_{H+}$) *vs*. excess acidity for 2-furaldehyde in aqueous sulfuric acid at 25 °C.

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*	ΔpK_{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

※ $\Delta pK_{BH+} = (pK_{BH+})_H - (pK_{BH+})_X$

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 H_2O.[4]

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.[4]

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).

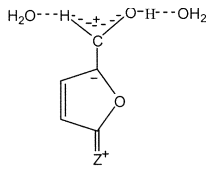
$$pK_{BH^+} = -11.63 \pm 0.63\ m^* + 1.93 \pm 0.29\ (r = 0.997) \quad (4)$$

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 = CH) is provided by the relatively low delocalizability of the oxygen atom in the hetero ring toward the carbonyl group. Theoretical analyses[7] at the MP2/6-31G* level[8] 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]



#4

The strong solvation of the BH^+ forms with donor ($\sigma_Z 0$) 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 (R = CH in **#1** and **#2**) as well as unhindered (R = H) benzoic acids (Y = OH),[1f] acetophenones (Y = CH_3),[3] methyl benzoates (Y = OCH_3)[1b,c] and benzamides (Y = 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.

Acknowledgment. This paper was supported by a basic data research fund of the Dong-A University in 2001.

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