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EFFECT OF SUBSTITUENTS ON INTRAMOLECULAR HYDROGEN BONDS OF 2-HYDROXY-5-SUBSTITUTED ACETOPHENONES

Zen-ichi Yoshida and Masami Haruta
Department of Synthetic Chemistry, Kyoto University
Yoshida, Kyoto, Japan

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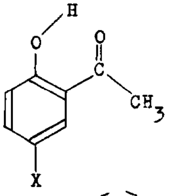
The spectroscopic study of intramolecular hydrogen bonds of a large number of compounds was developed by Wulf et al (1). They showed that the change in frequency of vibration occurs at about 7000 cm^{-1} (in wave-number units) corresponding essentially to the stretching of O-H and N-H bonds in molecules containing these groups. Cullinane and his co-workers (2) reported that the carbonyl stretching modes in o-hydroxy aromatic ketones were shifted to lower frequencies by conjugate chelation.

On the other hand, Jaffe (3) pointed out the additivity of electronic effects of substituents, and Fuson (4) reported these effects with carbonyl stretching modes of substituted benzoic acids.

Now, we wish to report the electronic effects of substituents on intramolecular hydrogen bonds of 2-hydroxy-5-substituted acetophenones [I] and on group frequencies of some reference compounds involving p-substituted phenols and m- or p- substituted acetophenones.

The O-H stretching frequencies of p-substituted phenols (ν^{f}_{OH})

were much influenced by substituents, that is, the more electron withdrawing the substituents are, the lower the frequencies become.



[I]

X: H, CH_3, CH_3O, Cl, Br, NO_2

On the other hand the C=O stretching frequencies of m- or p-substituted acetophenones became higher with the electron withdrawal by the substituents. The effects of substituents on both stretching frequencies of O-H and C=O are respectively interpreted in terms of changes in electronegativities of hydroxyl oxygen and carbonyl carbon atoms corresponding to changes of the substituents, because O-H bond of p-substituted phenols is weakened and C=O bond of m- or p-substituted acetophenones is strengthened as the electron withdrawal by the substituents increase.

2-Hydroxy-5-substituted acetophenones which do not show the absorption bands due to free O-H bonds in the 3600 cm^{-1} region exhibit broad and weak bands at 3100-2900 cm^{-1}.

In this region, as Martin (5) reported, there are very complex patterns of C-H aromatic stretching vibrations which overlap with the interacted O-H frequencies (ν^b_{OH}). Therefore, assignment in this region is very difficult. However, having been examined deliverately with the aid of some reference compounds (Table 1), the new absorption bands of 2-hydroxy-5-substituted acetophenones were found out as shown in Table 2.

TABLE 1

The Infrared Absorption Frequencies of Refference Compounds

	Acetophenone	Toluene	p-Cresol	p-Chlorotoluene	m-Substituted acetophenone	
					NO_2	OH
Absorption frequency (cm^{-1})		2945		2950		
	2967	2973	2971		2966	2966
				2981		
	3008		3012(s)			
	3032	3026	3032	3031	3009	3011
	3040(s)					
	3064					
	3086	3083		3085		3083
	3102(s)	3102(s)	3108	3100(s)		

s: shoulder

TABLE 2

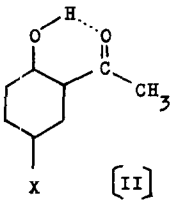
The Infrared Absorption Frequencies of 2-Hydroxy-5-substituted Acetophenone

	2-Hydroxy-5-substituted acetophenone					
	H	CH_3	CH_3O	Cl	Br	NO_2
Absorption frequency (cm^{-1})		2952	2954(s)			
	2978	2972		2976	2974	
						2992*
			3004			
	3017	3016		3014	3016	3012
		3033		3028*	3026*	
	3046*	3053(s)*	3050*			
		3062(s)		3064(s)	3064	
			3074(s)			
	3082(s)	3089		3087(s)	3078(s)	3089

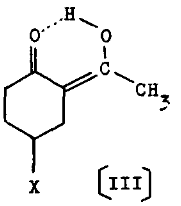
* : The new absorption band

Assuming that these new bands correspond to interacted O-H stretching frequencies (ν^{b}_{OH}) with oxygen atom of neighboring carbonyl group, the frequency differences ($\Delta\nu_{OH} = \nu^{f}_{OH} - \nu^{b}_{OH}$) were plotted against ordinary Hammett σ values. The best linear relationship has been established between values of $(\sigma_m + \sigma_p)/2$ and frequency shift ($\Delta\nu_{OH}$) as shown in Fig. 1.

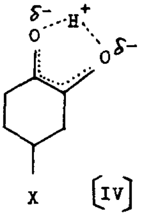
This linear relationship seems to indicate that intramolecular hydrogen bonding in 2-hydroxy-5-substituted acetophenones can be explained as an equivalent mixture of tautomeric structures [II] and [III] . As another interpretation for linear relationship between



[II]



[III]



[IV]

$\Delta\nu_{OH}$ and $(\sigma_p + \sigma_m)/2$, meso-ionic structure [IV] in which proton is situated at an equal distance from the both oxygens may be also possible. This structure is, however, denied from the following consideration: The structure [IV] implies that both aromatic carbon-oxygen bonds have a half double bond character. If 2-hydroxy-5-substituted acetophenones are expressed by the structure [IV] , therefore, it must be found that both absorptions corresponding to the stretching vibrations of C=O and C-O disappear and a new band corresponding to the stretching vibration of $C\overset{\cdot\cdot\cdot}{-}O$ half double bond is revealed in the 1400 cm^{-1} region expected from the force constant (8.4 X 10^{5} dynes/cm) of $C\overset{\cdot\cdot\cdot}{-}O$. The observation on infrared absorption spectra of [I] has

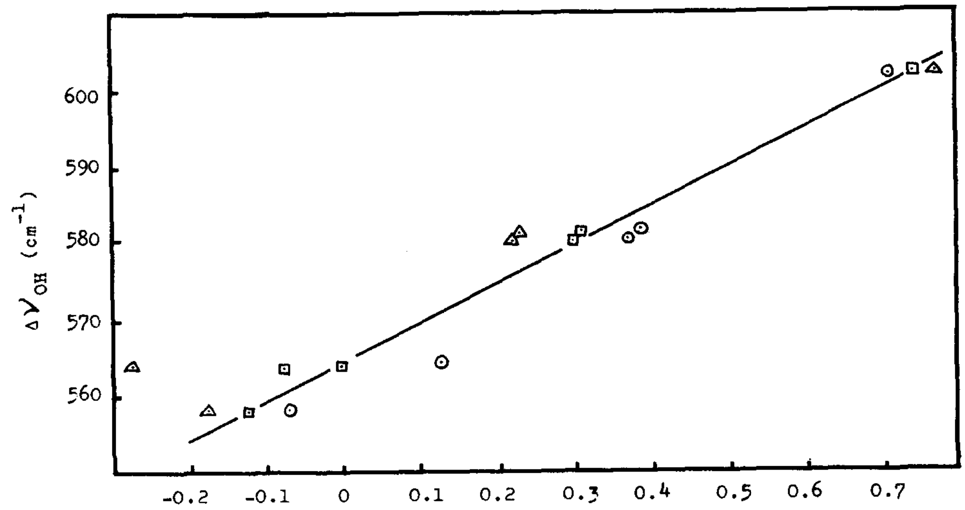


FIG. 1

The Relationship between $\Delta\nu_{OH}$ and Hammett σ Values.

△: σ_p ⊙: σ_m ⊡: $(\sigma_p + \sigma_m)/2$

shown that the hydrogen bonded carbonyl stretching vibration was found at 1648-1655 cm^{-1} but C···O stretching vibration was not. Furthermore assuming that $\Delta\nu_{OH}$ corresponds to the strength of the hydrogen bond, positive slope in Fig. 1 suggests that the intramolecular interaction between O-H and C=O group is enhanced by introducing an electron withdrawing group.

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