Intramolecular Hydrogen Bonding in α-Keto and α-Alkoxycarboxylic Acids. IV[1]*. Electronic Effect in Aryloxyacetic Acids*

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The authors measured[1,2] the O-H stretching (ν_{O-H}) and the C=O stretching ($\nu_{C=O}$) bands of various carboxylic acids and concluded that there is a hydrogen bonding in the acids carrying a hydrogen-accepting group at α-position. The hydrogen bonding is doubtlessly formed between the carboxylic hydroxyl group and the hydrogen-accepting group. Phenoxyacetic acid satisfies the above conditions and is found to exist as "free" and "bonded"[3] species, from the data obtained in O-H stretching and carbonyl regions.

The strength of the hydrogen-accepting power of the oxygen atom in the phenoxyl group may be assumed to be proportional to the electron density on the oxygen atom. Since it is known that Hammett's σ constants and the pK_a values of phenols are in linear relation, it can be seen that the σ constant[4] is a measure of the electron density of the oxygen atom in the aryloxy group. Thus the electron-repelling group will enrich the electron-density on the oxygen atom to be favorable as a hydrogen acceptor and the contrary situation is expected for the electron-attracting group.

The present paper deals with the effect of the substituent in the phenyl group on the ν_{O-H} and the $\nu_{C=O}$ absorptions, thus giving another verification for the existence of a hydrogen bonding between the carboxylic hydroxyl group and the hydrogen-accepting group at α-position.

Experimental

Preparation of the Materials. — Aryloxyacetic acids[5] were prepared in the following way. Equivalent amounts of sodium aryloxide and sodium chloroacetate in water were heated on a water bath for one to two hours. The reaction mixture was acidified and extracted with ether. The ethereal extract was shaken with aqueous sodium bicarbonate and the aqueous layer was acidified. The aryloxyacetic acid was recrystallized from benzene. Those which are not listed in Table I are known compounds and their physical constants agreed with the literature.

TABLE I. ARYLOXYACETIC ACID ($RC_6H_4OCH_2COOH$)

R	M. p. °C	Analyses			
		C, %		H, %	
		Found	Calcd.	Found	Calcd.
m-NO_2	151	48.80	48.74	7.19	7.11
p-Cl*	158.5	51.62	51.47	3.96	3.75
m-CH_3O	119	59.35	59.33	5.41	5.33
p-CH_3O	112	59.48	59.33	5.60	5.33

* Since the melting point (152°C) reported in the literature disagreed with that measured in this work, the purity was checked by elemental analysis.

Measurement and Calculation.—The measurement of the spectra were carried out with a Perkin Elmer 112G grating spectrophotometer. The materials were dissolved in carbon tetrachloride to make up concentration of ca. 0.002 mol./l. for the ν_{O-H} and ca. 0.0005 mol./l. for the $\nu_{C=O}$ measurements[6]. The spectral slit width was 1.0 cm^{-1} for the ν_{O-H} region and 0.6 cm^{-1} for the $\nu_{C=O}$ region. The absorption curves were assumed to be an overlap of the bands which obey the Lorentz function and the half band-widths ($\Delta\nu^{a}_{1/2}$) and the extinction coefficients (ε^{a}_{max}) at the maxima were obtained by Ramsay's first method[7]. That is, the approximate absorption maxima, $\Delta\nu^{a}_{1/2}$'s and ε^{a}_{max} were obtained by dividing the curves graphically and the characteristic numericals were corrected by the trial and error method.

Results and Discussion

Locations of the absorption maxima and the integrated intensities of the bands of aryloxyacetic acids are summarized in Table II.

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[1] Part III: M. Ōki and M. Hirota, This Bulletin, 34, 374 (1961).

[2] M. Ōki and M. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 81, 855 (1960).

[3] Although C. P. Smyth ("Dielectric Behavior and Structure", McGrawHill Book Co, Inc., New York (1955), p. 307) used the name cis and trans for the carboxyl group which has hydrogen atom between the two oxygen atoms and the other of which hydrogen atom is located outside the two oxygen atoms, respectively, "free" and "bonded" are used in this paper because of the nature of situation. However, as pointed out previously (Ref. 1), existence of a hydrogen bonding has been deduced in the cis form. Thus quotation marks are used to distinguish between the situation in this work and purely free form.

[4] H. H. Jaffé, *Chem. Revs.*, 53, 191 (1953).

[5] A. Michael, *J. Am. Chem. Soc.*, 9, 180 (1887).

[6] *p*-Nitrophenoxyacetic, *m*-nitrophenoxyacetic and *h*-benzyloxyphenoxyacetic acids were exceptions, of which poor solubility in carbon tetrachloride did not allow to measure at this level of concentration. The measurements of the nitro compounds were run with the saturated solutions.

[7] D. A. Ramsay, *J. Am. Chem. Soc.*, 74, 72 (1952).

TABLE II. THE ν_{O-H} ABSORPTIONS OF SUBSTITUTED PHENOXYACETIC ACIDS

Substituent	σ	ν_f, cm^{-1}	A_f**	ν_b, cm^{-1}	A_b**	$\Delta\nu_{max}$	A_b/A_f	log(10·A_b/A_f)	Concentration 10^{-3} mol./l.
p-NO_2	0.778	3521.8	—	not found	—	—	—	—	—*
m-NO_2	0.710	3522.3	—	3493.8	—	28.5	0.10	0.00	—*
m-Br	0.391	3522.5	7.59	3484.7	1.48	37.8	0.180	0.255	1.30
p-Br	0.232	3525.1	7.64	3494.0	2.95	31.1	0.386	0.587	0.828
p-Cl	0.227	3524.3	9.77	3492.8	2.58	31.5	0.264	0.422	1.09
m-CH_3O	0.115	3525.7	6.15	3484.0	2.60	41.7	0.426	0.629	1.71
H	0	3526.9	5.57	3487.5	2.69	39.4	0.484	0.685	1.18
m-CH_3	−0.069	3527.5	4.49	3486.7	3.15	40.8	0.698	0.844	1.47
p-CH_3	−0.170	3528.8	4.99	3484.5	3.48	44.3	0.699	0.845	1.60
p-CH_3O	−0.268	3527.7	4.72	3481.3	4.19	46.4	0.886	0.947	1.61
p-$C_6H_5CH_2O$	−0.41	3527.6	—	3482.4	—	45.2	0.993	0.997	—*

* Saturated solution.

** The integrated intensity can be calculated by the equation $A=2.30\times\frac{\pi}{2}\,\frac{1}{Cl}\log_{10}(T_0/T)_{max}\times\Delta\nu^a{}_{1/2}$, because the correction factors[7) are almost unity under the conditions for the measurement.

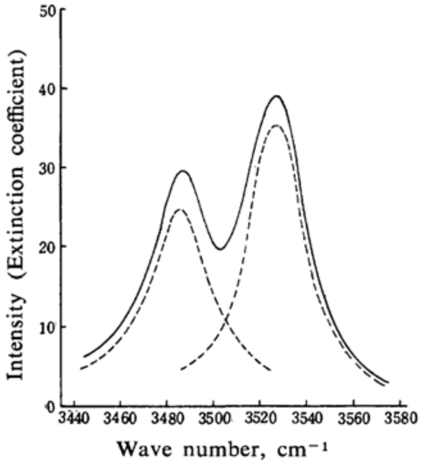


Fig. 1. The ν_{OH} absorption of m-methylphenoxyacetic acid.

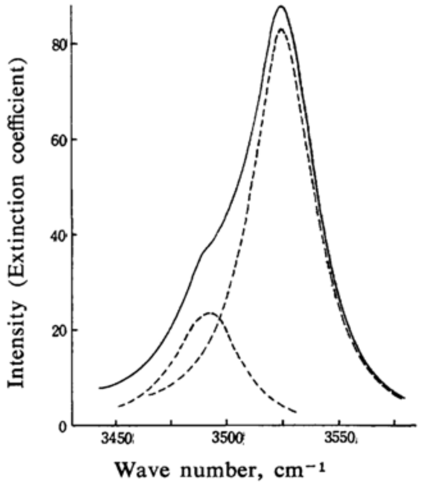
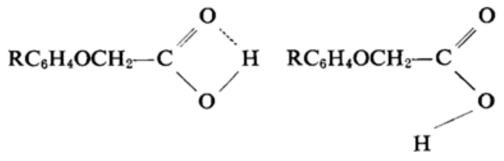


Fig. 2. The ν_{OH} absorption of p-chlorophenoxyacetic acid.

The aryloxyacetic acid with a substituent whose σ value is smaller than 0.115 (for meta-methoxyl) shows two apparent maxima, as exemplified by m-methylphenoxyacetic acid in Fig. 1. The separation of the two absorption maxima is fairly large. According to the previous paper, the band at ca. 3525 cm^{-1} is assigned to the cis structure (I) and the other at ca. 3490 cm^{-1} to the trans (II). Therefore, it can be said that the electron-repelling groups enhance the contribution of the trans, "bonded" form. If it can be assumed that the larger $\Delta\nu_{max}$ represents the more stabilization, then it is also clear that the aryloxyacetic acids carrying the electron-repelling group forms the more stable hydrogen bonding.



" free " structure I

" bonded " structure II

As to the substitution of the electron-attracting group, the aryloxyacetic acids do not show two maxima. p-Chlorophenoxyacetic and p-bromophenoxyacetic acids possess absorption bands with a peak and a shoulder as shown in Fig. 2, p-chlorophenoxyacetic acid being taken as a representative. m-Nitrophenoxyacetic acid shows a somewhat unsymmetrical absorption, while p-nitrophenoxyacetic acid a nearly symmetrical band. The error caused by the poor solubility of p-nitrophenoxyacetic acid prevents the division of the band into two.

The bands at higher and at lower wave numbers are undoubtedly assigned to the "free" and to the "bonded" OH's, respectively, as reported in the previous paper. Then it is evident that the electron repelling groups favor the "bonded" form and the electron-attracting groups the "free" form.

Since an equilibrium between the "free" and the "bonded" forms is considered to be operative, an equilibrium constant K_h may be expressed by Eq. 1.

$$K_h = \frac{[\text{bonded}]}{[\text{free}]} \qquad (1)$$

On the other hand, the concentrations of each of the species are proportional to the intensities of the respective ν_{O-H}, as far as Beer's law is applicable. Therefore, Eq. 1 may be transformed to

$$K_h = a\frac{A_b}{A_f} \qquad (2)$$

where A_b and A_f are the integrated intensities due to the "bonded" and the "free" molecules, respectively, and a is a constant pertaining to the magnifying power of the absorption intensity per molecule, when hydrogen bonding is formed. The value "a" is assumed to be equal for the series of compound.

Hammett's σ value is defined as

$$\sigma \equiv \log(K/K_0) \qquad (3)$$

where K_0 and K are dissociation constants of benzoic acid and the substituted benzoic acid, respectively. Thus a linear relation is expected between σ value and $\log(A_b/A_f)$ from Eqs. 2 and 3, because σ value is also a measure of the basicity of the oxygen atom in the aryloxyl group. The $\log(A_b/A_f)$ versus σ diagram is shown in Fig. 3 and the relation is linear as expected.

The frequency shift ($\Delta\nu_{max}$) from the "free" molecule to the "bonded" is also plotted against the σ value. The result (Fig. 4) may be considered as linear relation. The larger the the A_b/A_f value, the more is the $\Delta\nu_{max}$. Since it is accepted that the energy of a hydrogen bonding is proportional to the shift of the the wave number as a rough approximation, this $\Delta\nu_{max}-\sigma$ relation seems to be reasonable.

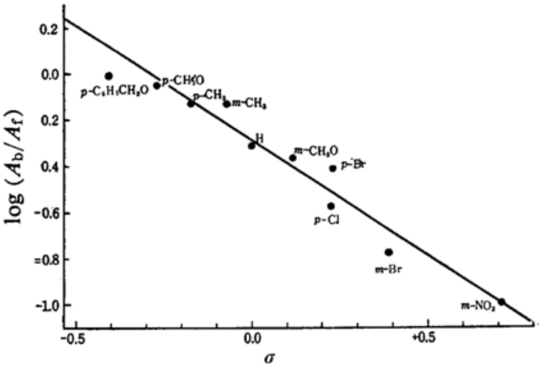


Fig. 3. The relation between the intensity ratio A_b/A_f and the Hammett's substituent constant.

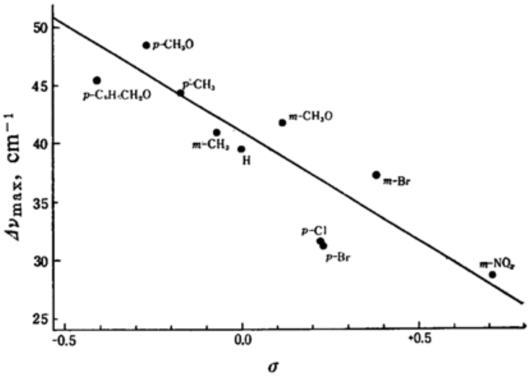


Fig. 4. The relation between the $\Delta\nu_{max}$ and the Hammett's substituent constant.

The measurement was extended to the carbonyl region and the band at 1790 cm^{-1} which is assigned[1] to the "bonded" form and the band at 1790 cm^{-1} which is assigned[1] to the "bonded" form and the other at 1760 cm^{-1} due to the "free" form are also found in every case.

Although these bands are nearly symmetrical, the dimer band at ca. 1730 cm^{-1} always overlaps with these, making it hard to obtain the integrated intensities. $\varepsilon_b/\varepsilon_f$ is obtained in this regard, where ε_b and ε_f are the extinction coefficients of the "bonded" and the "free" molecules at the corresponding peaks. The results are summarized together with other data in Table III. The result indicates that, when the σ value is large with a plus sign, $\varepsilon_b/\varepsilon_f$ is small and agrees with the tendency obtained in the ν_{O-H} measurement.

TABLE III. THE $\nu_{C=O}$ ABSORPTION OF ARYLOXYACETIC ACIDS

Substituent	$\nu_{C=O}$ of the "free" structure	$\nu_{C=O}$ of the "bonded" structure	$\varepsilon_b/\varepsilon_f$
m-NO$_2$	1768.9	1788.9	1.20
m-Br	1764.2	1789.8	1.19
p-Cl	1763.6	1790.2	1.27
H	1762.9	1790.6	1.37
p-CH$_3$	1763.0	1791.0	1.55
p-CH$_3$O	1760.5	1790.4	1.63

The ν_{O-H} band of the dimeric carboxylic acid is known to be a very broad band and is often masked by the ν_{C-H} band. However, the $\nu_{C=O}$ band of the dimetric acid is easily observable and it is known in this measurement that the contribution of the dimer is fairly large even in a dilute solution. From this result, the direct comparison of the absolute intensities of the bands corresponding to the "free" and the "bonded" forms becomes less significant. Thus, the ratio A_b/A_f or $\varepsilon_b/\varepsilon_f$ is exclusively used for the present discussion. The concentrations of the solutions are also included in Table III, because the contribution of the dimers may insert influence upon other data. The detailed discussion on the effect of concentration will be reported elsewhere in connection with the dissociation constant of the dimer.

Summary

The electronic effect on the hydrogen bonding formation in aryloxyacetic acid was examined. It is found that the electron-repelling groups enhance the band at the lower frequency in O–H stretching region and the band at ca. 1790 cm^{-1}. The result is completely agreeable with the expectation that the electron density on the oxygen atom in the aryloxyl group controls the hydrogen bonding formation.

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