

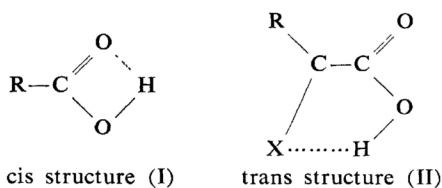
Intramolecular Hydrogen Bonding in α -Keto and α -Alkoxy-carboxylic Acids. III*. Comparison of the Spectra in the Carbonyl Region with Those in the O-H Stretching Region

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It was previously reported¹⁾ that the O-H stretching absorption of carboxylic acids with a proton accepting group at α -position, such as monoesters of oxalic acid, α -ketocarboxylic acid, α -alkoxy-carboxylic acid and α -aryloxy-carboxylic acid, had two maxima. The maximum at the higher frequency has been assigned to the free O-H stretching mode and the other at the lower frequency to the O-H of the hydrogen bonded form.

Since it is a well known fact that the C=O stretching absorption ($\nu_{C=O}$) shifts to the lower frequency on hydrogen bonding formation, the frequency shift of $\nu_{C=O}$ to the lower side is also expected in a carboxylic acid which forms hydrogen bonding. Alternately, a trans carboxyl group should show $\nu_{C=O}$ at the higher frequency, because the carbonyl group becomes free on hydrogen bonding formation between the carboxylic hydroxyl group and the hydrogen accepting group at α -position. In this respect, the authors measured $\nu_{C=O}$ together with the O-H stretching absorption (ν_{O-H}) and compared the spectra, thus establishing the assignment of the ν_{O-H} and $\nu_{C=O}$.



Experimental

Measurement and Calculation.—All spectral measurements were carried out with a Perkin Elmer 112G grating infrared spectrophotometer as a carbon tetrachloride solution. The absorption curves were regarded as an overlap of the bands with Lorentzian type envelopes and separated graphically. The half-width ($\Delta\nu_{1/2}$) and extinction coefficients at the absorption maxima (ϵ_{max}) are obtained by the above calculation and the apparent integrated intensities are obtained. The concentration of the solution is about 0.002 mol./l. for the measurements in the ν_{O-H} region and 0.0005 mol./l. for the $\nu_{C=O}$

region. The measurements are carried out through the ranges of 3580~3350 cm^{-1} for the ν_{O-H} region and 1830~1690 cm^{-1} for the $\nu_{C=O}$ region.

Materials.—The compounds used for the measurement are known unless otherwise described and their physical constants were checked prior to the measurements.

β -Phenoxypropionic Acid.—A solution of 250 g. (1.6 mol.) of β -phenoxyethyl chloride and 120 g. (1.85 mol.) of potassium cyanide in 600 ml. of ethanol was refluxed for four hours with stirring and the insoluble material was removed by filtration after cooling. The solvent was evaporated and the residue hydrolyzed by refluxing with 1000 ml. of 20% aqueous sodium hydroxide. The acidification followed by recrystallization from aqueous ethanol gave colorless leaves, m. p. 97°C, in 55% overall yield.

Found: C, 65.21; H, 6.30. Calcd. for $\text{C}_9\text{H}_{10}\text{O}_3$: C, 65.05; H, 6.07%.

γ -Phenoxybutyric Acid.—To a sodium ethoxide solution prepared from 38.5 g. (1.67 mol.) of sodium and 700 ml. of ethanol, was added 520 g. (3.3 mol.) of diethyl malonate followed by 260 g. (1.67 mol.) of β -phenoxyethyl chloride and the reaction mixture was refluxed for six hours. The solvent was evaporated and the residue poured into water. The organic material was taken up in ether, dried over anhydrous sodium sulfate and then fractionated. A fraction boiling at 195~200°C/16 mmHg was collected, being crude diethyl α -(2-phenoxyethyl)-malonate (360 g.), which was refluxed with 1100 ml. of 60% acetic acid containing 85 g. of sulfuric acid. The product was treated according to the literature²⁾. The acid was obtained as colorless needles, m. p. 64°C in 65% overall yield.

Found: C, 66.48; H, 6.75. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3$: 66.65; H, 6.71%.

Results and Discussion

Comparison in the Homologous Series.—The ν_{O-H} and the $\nu_{C=O}$ absorption spectra of some compounds are shown in Figs. 1 to 4 and the data obtained by assuming that the band envelopes are expressed by the Lorentz function are given in Table I.

Among the homologs of phenoxyacetic acid, the only compound which shows two ν_{O-H} maxima is phenoxyacetic acid. The band at

* Part II: This Bulletin, 33, 119 (1960).

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

2) E. B. Vliet, C. S. Marvel and C. M. Husen, "Organic Syntheses" Col. Vol. 2, John Wiley & Sons, New York (1943), p. 416.

TABLE I. THE ν_{O-H} AND THE $\nu_{C=O}$ ABSORPTION SPECTRA OF VARIOUS CARBOXYLIC ACIDS WITH HYDROGEN-ACCEPTING GROUPS

Compound	ν_{O-H} , cm^{-1}		$\nu_{C=O}$, cm^{-1}		
Phenoxyacetic acid	3526.9	3487.5	1790.6	1762.9	1737.4
β -Phenoxypropionic acid	3531.7	—	—	1760.8	1719.0
γ -Phenoxybutyric acid	3534.2	—	—	1760.0	1715.8
Methoxyacetic acid	3526.7	3450.8	1791.3	1761.3	1730.9
Isopropoxyacetic acid	3533.6	3437.4	1787.6	1760.8	1731.7
<i>tert</i> -Butoxyacetic acid	3528.0	3424.2	1788.5	1759.3	1733.3
α -Phenoxypropionic acid	3526.3	3475.1	1785.7	1758.7	1731.4
α -Phenoxyisobutyric acid	3526.3	3431.6	1786.1	1754.4	1716.4
Pyruvic acid	—	3430.7	1788.5	—	1725

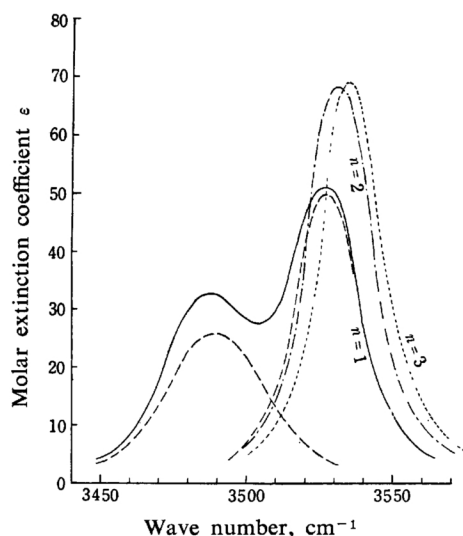


Fig. 1. The ν_{O-H} bands of $C_6H_5O \cdot (CH_2)_nCO_2H$
 $n=1$ — $n=2$ - - - $n=3$
 The curve of phenoxyacetic acid is separated into the two symmetrical absorptions. (---)

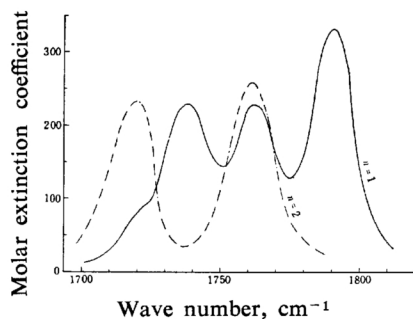


Fig. 2. The $\nu_{C=O}$ absorptions of $C_6H_5O(CH_2)_n \cdot CO_2H$. $n=1$ — $n=2$ - - -

higher frequency has been assigned to the ν_{O-H} of the monomeric acid, whereas the band at lower frequency has been assigned to the monomeric acid with an intramolecular hydrogen bonding. The higher homologs exhibit one band at ca. 3530 cm^{-1} which can doubtless be assigned to the usual ν_{O-H} mode of mono-

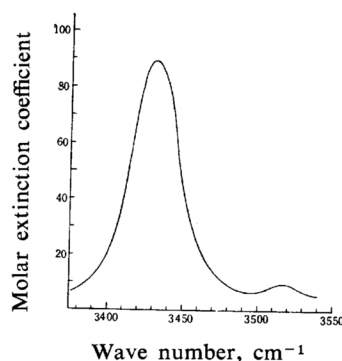


Fig. 3. The ν_{O-H} absorption of pyruvic acid.

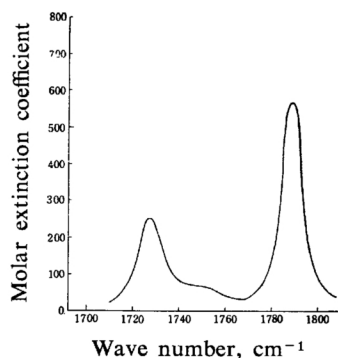


Fig. 4. The $\nu_{C=O}$ absorption of pyruvic acid.

meric acid. The results are indicative of the absence of hydrogen bonding between the carboxylic hydroxyl group and the oxygen atom of the phenoxyl group in β -phenoxypropionic and γ -phenoxybutyric acids.

In the carbonyl region, phenoxyacetic acid shows three maxima and a shoulder at ca. 1715 cm^{-1} , while β -phenoxypropionic and γ -phenoxybutyric acids exhibit only two bands. Acetic acid and benzoic acid also possess similar absorptions with the latter two compounds. Comparison of these data together with the study of the change in concentration as described later indicates that the band at about 1760 cm^{-1} is arising from the *cis* structure of

TABLE II. COMPARISON OF THE SPECTRA OF CARBOXYLIC ACIDS CARRYING α -HYDROGEN ACCEPTING GROUPS WITH THOSE OF THEIR ESTERS

Compound	R	$\nu_{C=O}$, cm^{-1}			
CH_3COCOOR	$\begin{Bmatrix} \text{H} \\ \text{Ethyl} \end{Bmatrix}$	1788.5	—		$\begin{matrix} 1725 \\ 1733.0 \end{matrix}$
$\text{C}_6\text{H}_5\text{OCH}_2\text{COOR}$	$\begin{Bmatrix} \text{H} \\ \text{Ethyl} \end{Bmatrix}$	1790.6	$\begin{matrix} 1762.9 \\ 1766.8 \end{matrix}$		$\begin{matrix} 1737.4 \\ 1739.4 \end{matrix}$
$\begin{matrix} \text{COOR} \\ \\ \text{COOCH}_3 \end{matrix}$	$\begin{Bmatrix} \text{H} \\ \text{Methyl} \end{Bmatrix}$	1808.2	$\begin{matrix} 1788.9 \\ 1780.2 \end{matrix}$	$\begin{matrix} 1758.3 \\ 1752.3 \end{matrix}$	$\begin{matrix} 1739.9 \\ \end{matrix}$
$\text{C}_6\text{H}_5\text{COOR}$	$\begin{Bmatrix} \text{H} \\ \text{Ethyl} \end{Bmatrix}$	—	1744		$\begin{matrix} 1700 \\ 1722.6 \end{matrix}$
CH_3COOR	$\begin{Bmatrix} \text{H} \\ \text{Ethyl} \end{Bmatrix}$	—	$\begin{matrix} 1769.3 \\ 1754 \end{matrix}$		1714.8

a monomeric carboxylic acid illustrated by I, whereas the band at 1790 cm^{-1} must correspond to the trans structure.

The difference ($\Delta\nu_{\text{max}}$) of the wave number between the band maxima corresponding to the cis and the trans structures is about 30 cm^{-1} and may be explained in the following way. That is, the peak for the cis isomer shifts to the lower frequency because of the formation of the hydrogen bonding between the carboxylic hydroxyl and carbonyl groups, a non-planar³⁾ four-membered ring being formed. Although this may be taken as a peculiar phenomenon, a support is found in the accumulated data in this laboratory⁴⁾. None of the phenylacetic, diphenylacetic and triphenylacetic acids show intramolecular interaction between the hydroxyl group and π -electrons, the existence of which is naturally expected from the analogy of *N*-methylphenylacetamide⁵⁾. The absence of the interaction must be interpreted by considering that there is a favorable structure over the intramolecular O—H \cdots π interaction, the energy of which is estimated as about 1 kcal./mol. The stabilization may be afforded by the presence of O—H \cdots O=C hydrogen bonding in the cis structure of the carboxylic acid.

The homologs of methoxyacetic acid which carries methyl groups show some variation in the $\nu_{C=O}$ absorptions according to the degree of substitution. Although the authors cannot comment precisely on the cause of the variation at the present time, it is probable that the electronic effect of the introduced methyl groups is playing an important role.

Pyruvic acid possesses two peaks at 1788.5 cm^{-1} and 1725 cm^{-1} and a shoulder at 1735 cm^{-1} but the band at 1760 cm^{-1} which is

common for the other acids failed to appear. This is reasonable, since the band at 1760 cm^{-1} corresponds to the cis species, the absorption of which in the ν_{O-H} region is negligibly small. The band at the highest frequency is assigned to the free carbonyl group of the carboxyl group which is due to the hydrogen bonding formation between the carboxylic hydroxyl and the α -carbonyl groups. The origin of the two bands at the lower frequencies is determined through the study of concentration effects on the intensities. The band at 1735 cm^{-1} is assigned to the dimeric carboxyl group and the other at 1725 cm^{-1} to the α -carbonyl group.

It is well known that the α -ketocarboxylic acid has the monomer $\nu_{C=O}$ absorption at abnormally high frequency. The phenomenon has been attributed to the inductive and the field effects of the α -keto group. However, it is now evident that pyruvic acid exclusively exists as the trans monomer with the free carbonyl group of the carboxyl group which causes the absorption at the high frequency.

Comparison of the Spectra of the Acids with those of the Esters.—In Table II are listed the $\nu_{C=O}$ spectra of esters together with the corresponding acids. Since the esterification cancels all possibilities of hydrogen bonding, esters of the carboxylic acids which carry the hydrogen accepting group at α -position are expected to be normal when compared with the ordinary esters and this is proved to be the case. None of the esters show $\nu_{C=O}$ band as high as 1790 cm^{-1} .

Ethyl pyruvate shows one somewhat asymmetrical $\nu_{C=O}$ band at 1733 cm^{-1} , which is believed to be an overlap of the ester and ketone bands. The band intensity is nearly twice that of the normal esters. Ethyl phenylacetate possesses two absorptions in the carbonyl region, the intensities being nearly equal. This phenomenon may be attributed to the

3) C. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill Book Co., Inc., New York (1955), p. 306.

4) H. Iwamura, unpublished work.

5) I. Suzuki, M. Tsuboi and T. Shimanouchi, *Spectrochim. Acta*, **16**, 467 (1960).

TABLE III. THE EFFECT OF THE CONCENTRATION ON THE INTENSITIES OF THE ABSORPTION BANDS OF PHENOXYACETIC ACID

Concentration mol./l.	Intensity of the absorption band			
	$\nu_{C=O}$ of the trans structure of the monomer (ϵ_t) at 1790.6 cm^{-1}	$\nu_{C=O}$ of the cis structure of the monomer (ϵ_t) at 1762.9 cm^{-1}	$\nu_{C=O}$ of the dimer at 1737.4 cm^{-1}	ϵ_t/ϵ_c
0.00092	204	153	281	1.33
0.00046	248	185	252	1.34
0.00023	300	226	221	1.33
0.000058	390	278	185	1.40

existence of the rotational isomers or to some other cause. The decisive comment cannot be made at the present stage.

The Effects of Concentration on the $\nu_{C=O}$ Bands of Phenoxyacetic Acid.—As was already pointed out, phenoxyacetic acid possesses three $\nu_{C=O}$ bands, the intensities of which are measured at various concentrations in carbon tetrachloride. The results are shown in Table III.

It is recognized that the intensities of the bands at 1762.9 cm^{-1} and 1790.6 cm^{-1} increase with the decreasing concentration, while the band at 1737 cm^{-1} decreases on lowering the concentration. These behaviors indicate that two bands at the higher frequencies must be attributed to the monomeric forms of the carboxylic acid and the other at 1737 cm^{-1} to the dimeric form. It is also found that the ratio of the intensities of the bands at 1762.9 cm^{-1} and 1790.6 cm^{-1} is almost constant at the various concentrations. This fact suggests that the equilibrium between the cis and the

trans forms is not influenced by the concentration.

Assignment of the Band.—From the above discussion, it is apparent that the bands can be assigned as shown in Table IV.

Summary

The $\nu_{C=O}$ and the ν_{O-H} absorption of carboxylic acids were measured and the following conclusion was obtained; 1) The carboxylic acids carrying a proton-accepting group at α -position give three absorption bands at ca. 1790 cm^{-1} , ca. 1760 cm^{-1} and 1740~1710 cm^{-1} , which can be assigned to the trans form of the monomeric acid, the cis form of the monomeric acid and the dimer, respectively. 2) The $\Delta\nu_{\text{max}}$ between the cis and the trans forms can be explained from an intramolecular hydrogen bonding between carboxylic hydroxyl and carbonyl groups.

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TABLE IV. ASSIGNMENT OF THE ν_{O-H} AND THE $\nu_{C=O}$ BANDS OF A CARBOXYLIC ACID WITH AN α -HYDROGEN-ACCEPTING GROUP

Structure	Monomer		Dimer cm^{-1}
	Cis structure cm^{-1}	Trans structure cm^{-1}	
ν_{O-H}	3550~3500	3490~3390	3300~2500
$\nu_{C=O}$	ca. 1760	ca. 1790	1730~1710