The Infrared Dichroism and Molecular Orientation of Modifying Reagents, L-β-Phenyllactic Acid and L-β-Phenyl-α-alanine, in Thin Films on Nickel Metal Surfaces

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The infrared absorption spectra of thin films of modifying reagents, L-β-phenyllactic acid and L-β-phenyl-α-alanine, formed on nickel metal plates were measured by the high-sensitivity reflection method. From the infrared dichroism in the reflection spectra, the molecular orientations in the thin films were deduced. The C=O and alcoholic O–H bonds of L-β-phenyllactic acid are oriented nearly vertical to the metal surface, whereas the carboxyl O–H bond and the benzene ring are parallel to the surface. The benzene ring and the C–N bond in L-β-phenyl-α-alanine are oriented nearly parallel to the metal surface, while the O···O axis of the carboxylate group is inclined to the surface.

Infrared spectroscopy has been extensively applied to the study of surface phenomena. For example, the adsorption of gaseous molecules on metal surfaces has been often investigated by employing transmission methods.[1] On the other hand, the method of reflection using a beam polarized parallel to the plane of incidence at high incident angles (the high-sensitivity reflection method) has facilitated the spectral investigation of surface phenomena on bulk metal surfaces because of its high sensitivity, which, in turn, results from the enhanced intensity of the oscillating electric field normal to the reflecting metal surface.[2] The spectrum of thin film on a metal mirror obtained by this method is a faithful reproduction of the absorption spectrum if the film is isotropic and consists of organic compounds.[3] When the film is anisotropic, the reflection spectrum shows infrared dichroism, and the relative intensities of the infrared bands can be used to deduce the molecular orientation in the film.[4] Because of these advantages, the high-sensitivity reflection method has been successfully used in the investigations of the chemisorption on clean metal surfaces,[5,6] the polymorphism[7] and molecular orientation[8] in thin films on metal surface, and the oxidation and corrosion inhibition of metals.[9]

In recent years, a new type of asymmetric synthesis has been studied by Izumi and his co-workers using a Raney nickel catalyst modified by certain optically active compounds.[10] They have found that the hydrogenation of methylacetoacetate over Raney nickel modified with optically active hydroxy or amino acids affords a definite optical isomer of methyl-β-hydroxybutyrate, its identity depending upon the optical activity of the compound used as the modifying reagent.[10] While the mechanism is still uncertain, it is worth noting that the effective modifying reagents available for such an asymmetric reduction are limited to optically active acids in which a OH or NH_2 group is attached at the asymmetric carbon atom. Therefore, it seems most likely that the geometry of the modifying reagent adsorbed on the Raney nickel catalyst plays an important role in the determination of the optical isomer of the reduction product. Hence, a particular interest is focused on the molecular orientation of modifying reagents on the Raney nickel catalyst.

The epitaxial growth of an organic crystal occurs on a single crystal when the organic molecule is adsorbed strongly on the crystal, and the molecular orientation in the overgrowing crystal correponds to the state of the adsorbed molecule.[11] Tanabe and Uyeda investigated the thin film of L-β-phenyl-α-alanine, formed from an aqueous solution on nickel film, by electron microscopy and diffraction, and suggested that this molecule is in a certain state of oriented adsorption at the interface.[12] However, they could not determine the orientation of the molecules because the crystal structure of L-β-phenyl-α-alanine was unknown.

The present study was undertaken in the hope of making clear the orientations of the modifying reagents, L-β-phenyllactic acid and L-β-phenyl-α-alanine, in thin crystal films formed on nickel surfaces, using the high-sensitivity reflection technique.

Experimental

The infrared spectra were taken by means of a JASCO model IR-G spectrophotometer equipped with a JASCO PR-1 assembly designed for use in a single-beam reflection operation.[4] In this method, however, the weak absorptions are subjected to interference from atmospheric water vapor. This problem was solved by the combined use of signal averaging and back-ground elimination procedures.[5] The calculations were performed on a JEOL model JEC-5 spectrum computer. The modifying reagents of L-β-phenyllactic acid and L-β-phenyl-α-alanine were prepared and supplied by the Institute for Protein Research, Osaka University, and were used without further purification. In the present study, an electrolytical nickel (99.9% purity) plate was used as substrate and mirror. To obtain a high reflectivity, the nickel plate was polished with silicon carbide and chromium oxide to reduce its roughness to a minimum. After having been treated with a 20% NaOH solution at 80 °C and having been rinsed in distilled water, the nickel plate was immersed into a 0.5% aqueous solution of a modifying reagent. The sample of the modified nickel plate was dried in air and was then subjected to the reflection measurement. A thin film of fine crystallites of the reagent was formed on the metal substrate upon the evaporation of the water.

Results and Discussion

L-β-Phenyllactic Acid. The absorption spectrum of this compound, $C_6H_5CH_2CH(OH)COOH$, in the randomly oriented state and the assignment of the absorp-

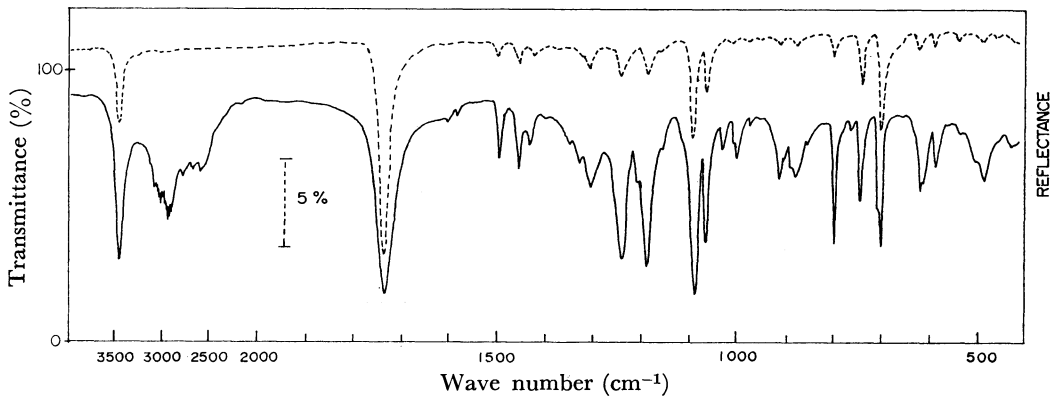

Fig. 1. Infrared absorption spectra of L-β-phenyllactic acid.
——: Transmission spectrum of powdered crystal (KBr disk).
·····: High sensitivity reflection spectrum of the thin film formed on nickel metal surface.

tion bands must be available if its reflection spectrum is to be discussed. For this purpose, the transmission spectrum of L-β-phenyllactic acid (PLA) was measured by the KBr disk method in the region of 400—4000 cm^{-1}. The spectrum thus obtained is shown in Fig. 1. The assignment, to be described below, is mainly based on comparison with the spectra of such related compounds as the sodium salt and *O*-deuterated compound of PLA, and DL-mandelic acid, its sodium salt, and its *O*-deuterated compound. The most important vibrational bands of PLA and its sodium salt are collected in Table 1. PLA shows a strong absorption at 3450 cm^{-1} and two broader absorptions centered around 2920 and 2570 cm^{-1}, all of which shifted to lower frequencies upon deuteration, as is shown in Table 1; these can be assigned to O–H stretching vibrations. The sodium salt of PLA shows a strong band at 3400 cm^{-1} and a weaker band at 3150 cm^{-1}, while no other band appears over the lower O–H stretching region. Therefore, the strong band at 3450 cm^{-1} observed with PLA is evidently due to the alcoholic O–H stretching, and the remaining broad bands in the lower-frequency region, to the carboxyl O–H stretchings. The strong absorption band observed at 1725 cm^{-1} can easily be assigned to the C=O stretching. The weak and narrow bands at 1500 and 1453 cm^{-1} of PLA are observed also for DL-mandelic acid and other related compounds, so these bands are assigned to the in-plane skeletal deformation of the benzene ring. The strong bands observed in the 1050—1300 cm^{-1} region are attributable to the C–O–H fragments. From the vibrational character, these bands involve the interacting in-plane deformation vibration of the C–O–H angle and the stretching one of the C–O bond, giving rise to two bands.[13] In PLA, there are two pairs of deuteration-sensitive bands, at 1245 and 1197, and at 1093 and 1070 cm^{-1}. The former pair disappears upon the change from –COOH to –COONa, while the latter shows no appreciable change. Therefore, we assigned the two bands at 1245 and 1197 cm^{-1} to the vibrations of the carboxylic C–O–H group, and the other pair, to alcoholic C–O–H. The intense bands at 708 (sh) and 700 cm^{-1} are assigned to the CH out-of-plane deformation or the skeletal deformation vibration of the benzene ring. These assignments are mainly based on the fact that the bands remain unshifted on the deuterations of O–H groups. The spectrum of mandelic acid changed with the deuteration and salt formation in the same manner as in the case of PLA, supporting the above-mentioned assignment.

Table 1. Infrared frequencies (cm^{-1}) and assignments of L-β-phenyllactic acid and its sodium salt (KBr disk)

$C_6H_5CH_2$–CHCOOH (OH)	$C_6H_5CH_2$–CHCOO⁻Na⁺ (OH)	Assignments
3450 (2540) s	3400 (2500) s 3150 (2320) w	alcoholic O–H str.
2920 (2200) m 2570 (2030) w		carboxyl O–H str.
1725 s		C=O str.
	1597 sh 1580 s	COO^- antisym. str.
1500 w	1497 w	phenyl ring def.
1453 w	1455 sh	phenyl ring def.
	1402 m	COO^- sym. str.
1245 (1085) s 1197 (1054) s		carboxyl C–O–H
1093 (935) s 1070 (917) m	1090 (932) sh 1080 s	alcoholic C–O–H
708 sh 700 s	700 s	phenyl C–H out-of-plane def.

s: strong, m: medium, w: weak, sh: shoulder.
Values in parentheses correspond to the peaks of *O*-deuterated compounds.

The high-sensitivity reflection spectrum of the thin PLA film formed on a nickel metal surface is shown in Fig. 1. The absorption bands of the thin film appear at essentially the same frequencies as in the transmission spectrum of the bulk crystals. However, differences in relative intensities are noticed between the thin film and the bulk crystals. Because no new band appeared in the reflection spectrum, the thin film probably did not contain any compound other than PLA in any appreciable quantity. The spectral change, therefore, can be interpreted in terms of a molecular orientation in the thin film, as has been discussed in previous papers.[4,5,8] In the high-sensitivity reflection method employed in the present work, the oscillating electric vector of radiation in the vicinity of the reflecting

surface is practically polarized normal to that surface.[2] Therefore, any spectral change in the band intensities can reveal information about the direction of the transition moments of the molecule; moreover, if the molecular structure in the solid phase is known, the molecular orientation as a whole may also be obtained. On the basis of the assignments mentioned above, the orientation of PLA to the nickel metal surface can be determined by comparing the thin film spectrum with the bulk one. In the thin film spectrum shown in Fig. 1, it can clearly be seen that the O–H stretching band of the carboxyl group almost disappears, while the alcoholic O–H stretching band appears strong. The bands arising from the C–O stretching and C–O–H in-plane deformation vibrations of the carboxyl group appear at almost the same frequencies as that in the bulk spectrum. In addition, it is quite likely that the carboxyl O–H group is hydrogen-bonded in crystalline phases. Therefore, the disappearance of the carboxyl O–H stretching band can not be ascribed to the dissociation of the hydrogen bond between carboxyl groups. These facts indicate that the carboxyl O–H bond is aligned nearly parallel to the nickel substrates, while the alcoholic O–H bond is not. On the other hand, the band due to the C=O stretching vibration of the carboxyl group has the highest absorption intensity in the thin film spectra; hence, the transition moment and, therefore, the C=O bond are considered to be perpendicular to the nickel metal surface. Accordingly, the molecule is probably oriented in such a way that the plane containing a carbon and two oxygen atoms of the carboxyl group is perpendicular to the nickel metal surface.

Another marked difference between the bulk and the thin film crystal is seen in the bands of the 1050—1300 cm^{-1} region due to the vibrations of the carboxyl and alcoholic C–O–H groups; *i.e.*, the bands arising from the former group lose much of their intensity in the thin film, while the bands of the latter are unchanged. In view of the fact that the C–O–H bands represent the interacting C–O stretching and in-plane O–H deformation vibrations, the observed results support the different alignments for the carboxyl and alcoholic O–H bonds mentioned above.

On the other hand, the crystal structure of *p*-bromo-L-*β*-phenyllactic acid was investigated by Kakudo *et al.*; the molecular conformation in the crystal is shown in Fig. 2.[14] Therefore, the determination of the molecular orientation as a whole can most conveniently be performed by assuming that the molecular conformation of *p*-bromo-L-*β*-phenyllactic acid is applicable to the

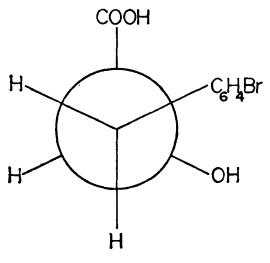

Fig. 2. Molecular conformation of *p*-bromo-L-*β*-phenyllactic acid, as viewed along the C_β—C_α bond.[14]

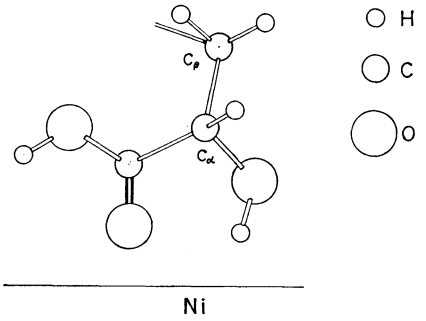

Fig. 3. Molecular orientation in thin L-*β*-phenyllactic acid crystal formed on nickel metal surface. The phenyl group is omitted from the figure.

case of PLA. The derived orientational model for thin PLA in crystal is shown in Fig. 3. In the thin film spectrum, the band at 700 cm^{-1} assigned to the CH out-of-plane deformation or skeletal deformation of the benzene ring remains as a strong band, while the bands assigned to the in-plane skeletal deformation of the benzene ring observed at 1453 and 1500 cm^{-1} decrease in relative intensity. These observations indicate that the plane of the benzene ring is aligned rather parallel to the nickel substrate.

The thickness of the films formed by the procedure described above is estimated from the band intensity in the reflection spectra to be a few hundred angstroms. The reflection spectra of films with such a thickness scarcely provide any direct information about the species chemisorbed on the nickel surface. However, the orientation of molecules in a thin film is governed by the orientation of the species which are adsorbed strongly on the substrate surface and which act as the nuclei of crystal growth.[11] The orientation of the PLA molecule in the film may, therefore, correspond to that of species strongly adsorbed on the nickel surface and playing an important role in the above-mentioned catalytic hydrogenation.

L-β-Phenyl-α-alanine. It is well known that L-*β*-phenyl-α-alanine exists in a crystal as a zwitter ion such as

$$C_6H_5CH_2\text{–}\underset{\displaystyle NH_3^+}{\underset{|}{CH}}\text{–}COO^-$$

As a result, it has the absorptions of an ionized carboxyl group and an NH_3^+ ion. Therefore, the important part of these characteristic bands can be expected to appear between 1400 and 1700 cm^{-1}, by analogy with other amino acids.[15] Figure 4 shows the transmission spectra of L-*β*-phenyl-α-alanine and its *N*-deuterated species, obtained by the KBr disk method in the region from 1400 to 1700 cm^{-1}. The strong three bands at 1500, 1565, and 1628 cm^{-1}, which disappear on *N*-deuteration, as is shown in Fig. 4, may be regarded as the bands due to the vibrations of the NH_3^+ group. The bands at 1410 and 1602 cm^{-1}, which remain unchanged on *N*-deuteration, can be assigned to the CO_2^- symmetric and anti-symmetric stretching vibrations respectively. The bands at 1500 and 1628 cm^{-1} can be assigned to the NH_3^+ symmetric deformation and degenerate deformation respectively by referring

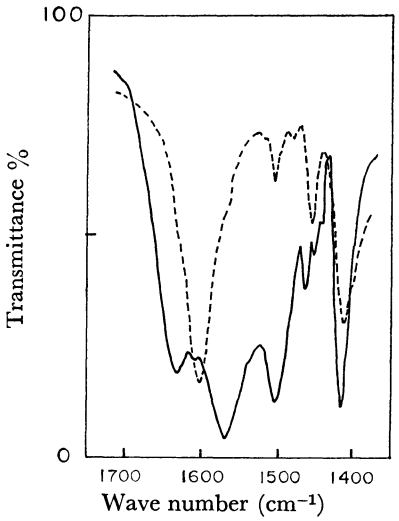

Fig. 4. Transmission spectra of L-β-phenyl-α-alanine (solid line) and its *N*-deuterated species (broken line).

to the assignments for DL-β-phenyl-α-alanine.[16] However, there is a marked difference between the spectrum of L-β-phenyl-α-alanine and that of DL-β-phenyl-α-alanine; the 1565 cm^{-1} band is present only in the former. This band is also observed with D-β-phenyl-α-alanine. According to Tsuboi *et al.*,[15] it is most likely that this band arises from the breaking down of the C_{3v} symmetry of the NH_3^+ group. Except for the 1565 cm^{-1} band, the spectrum of L-β-phenyl-α-alanine is identical with the spectrum of the DL-form, apart from slight shifts; hence, no further descriptions of it will be given.

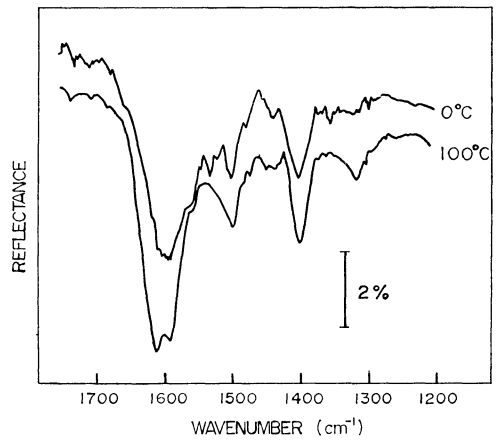

Fig. 5. High sensitivity reflection spectra of thin L-β-phenyl-α-alanine crystals formed on nickel metal surfaces. The temperature refers to the modifying temperature at which the sample was prepared.

Figure 5 shows the high-sensitivity reflection spectrum of the thin L-β-phenyl-α-alanine (L-phenylalanine) film formed on nickel metal surfaces at different modifying temperatures. The spectrum of the thin film is compared with that of the non-oriented sample obtained by using the KBr technique, as in the case of PLA. The thin film spectra show infrared dichroism, which is caused by the preferred orientation in the film; they correspond well to the results obtained by electron-optical methods.[12] The most remarkable feature is the weakness of the NH_3^+ band at 1565 cm^{-1} in the thin film spectra, irrespective of the modifying temperature. This change in intensity may be ascribed to the orientation of the NH_3^+ group, for another NH_3^+ deformation band appears at about 1610 cm^{-1} in the thin film. Another striking difference between the thin film and bulk crystals is seen in Fig. 5; the band at 1500 cm^{-1} due to the symmetric deformation of the NH_3^+ group remarkably decreases in intensity. This may be attributed to the molecular orientation in the thin L-phenylalanine crystal. In view of the fact that the vibrational mode of the NH_3^+ symmetric deformation has a transition moment along the C–N bond, it may be concluded that the C–N bond lies nearly parallel to the nickel substrate.

The most important bands yet to be discussed are those of the CO_2^- stretching vibrations appearing at 1400 and 1600 cm^{-1} in the thin films. It can be seen from Figs. 4 and 5 that the intensity of the band due to the CO_2^- symmetric stretching relative to that of the CO_2^- anti-symmetric stretching decreases with the change from the bulk crystals to the thin film. Considerations of these vibrational modes and the corresponding changing dipole moments provide a possible orientation for the CO_2^- group.

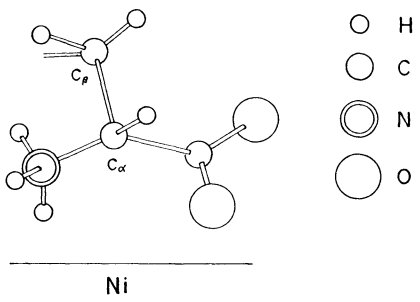

Fig. 6. Molecular orientation of thin L-β-phenyl-α-alanine film formed on nickel metal surface. The phenyl group is omitted from the figure.

No remarkable spectral change is found in the region below 1400 cm^{-1} except for the intensified bands at 700 and 740 cm^{-1}. Since these bands represent the out-of-plane deformations of the benzene ring, the above-mentioned results show the parallel orientation of the benzene ring to the nickel surface. Consequently, the most probable orientation is proposed by assuming that the molecular conformation obtained by X-ray work[14] is valid even for the thin film of the L-phenylalanine. The orientation model of the L-phenylalanine molecule in the thin film crystal is shown in Fig. 6. The aspect of the orientation is compatible with that obtained for α-alanine, so far as the common fragment is concerned,[12,17] suggesting that the nature of interaction between the molecule and nickel substrate is the same for both compounds.

The optical activity of the reaction product of catalytic hydrogenation changes with a change in the modifying temperature.[10] This change may be caused by the change in the posture of the modifying reagent on the nickel surface. The relative intensities of the bands

at 1322 and 1610 cm^{-1} in the thin-film spectra change with the modifying temperature, as can be seen in Fig. 5. This change may be attributed to the different molecular orientations in the films and may correspond to the change in the orientation of the species strongly adsorbed on the nickel surface. However, the results obtained are not sufficiently accurate, partly because of the interference from absorptions due to water vapor, to enable us to discuss the change in the orientation of the surface species with the temperature; any discussion must, therefore, be postponed until further information is available.

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