# Infrared Dichroism and Molecular Orientation of Ethyl 2-Hydroxyimino-3-oxo-3-phenylpropionate in Thin Films on Pd Metal Surfaces

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The infrared absorption spectra of ethyl 2-hydroxyimino-3-oxo-3-phenylpropionate, in differently oriented films, formed on Pd metal plates, were measured by using the high-sensitivity reflection method. The thin crystal film **A** was formed when the solvent was evaporated from the thin liquid film remaining on Pd. On the other hand, the film **B** resulted from the crystallization of the amorphous solid film which was initially formed on Pd when the liquid film was thick. From the infrared dichroism in the reflection spectra, the molecular orientations in thin films were obtained as follows. In the film **A**, the ketone C=O and C=N bonds are probably at a pseudo *s-cis* and are aligned in such a way that the C–C bond connecting the ketone carbonyl group with the C=N group are nearly parallel to the Pd surface. The NO bond is aligned parallel to the metal surface. The ester group is oriented nearly vertical to the metal surface, the C=O bond lying tilted to the surface. In the film **B**, the ester C=O and NO bonds are aligned nearly perpendicular to the Pd surface, while the ketone C=O bond is not so. The C···C axis of the ester is rather parallel to the surface. The orientation in the thin film **A** agrees well with the hypothetical chelation model.

The reflection infrared spectroscopy using the beam polarized parallel to the plane of incidence at high incident angles[1] (the high-sensitivity reflection method) is a very powerful tool of investigating various surface phenomena. The best known example is the absorption of gaseous molecules on metal surfaces.[2] In this method, the enhanced oscillating electric field normal to the metal mirror surface serves not only to detect the species adsorbed on the metal surface but also to obtain informations about the orientation of the adsorbed species.[3] This reflection method is also used successfully for the study of thin films of organic crystals formed on metal surfaces.[4] When an organic crystal is grown on a metal surface, the interaction with the metal surface may result in polymorphism or preferred orientation.[5] The preferred orientation and in particular the anomalous crystal structure are generally stable when the film is very thin. Since the crystal grows at the molecule strongly adsorbed on the substrate surface, which acts as the nucleous, the orientation of molecules in thin film crystal may be governed by that of the adsorbed molecule.[6,7] The orientation of adsorbed molecule may, therefore, be deduced from the infrared dichroism of thin crystal film.

On the other hand, the asymmetric synthesis of amino acids by hydrogenolytic asymmetric transamination using Pd hydroxide catalyst has been extensively investigated by one of the authors (Harada) and his co-workers.[8] They found that optically active α-amino acids could be synthesized from the Schiff base of α-keto acids or their esters with optically active α-alkylbenzylamines by catalytic hydrogenation and subsequent hydrogenolysis. In order to explain the reaction mechanism, Harada *et al.*[8] proposed the "chelate hypothesis" that the intermediate five membered cyclic complex[9] with a metal atom of the catalyst could be formed and then adsorbed on the catalyst surface. The intermediate complex assumed in elucidating the hydrogenation of ethyl 2-hydroxyimino-3-oxo-3-phenylpropionate is shown in Fig. 1.[10] Although there has been no direct evidence of the existence of such the chelate ring complex, it is perhaps reasonable to assume that an intermediate on the heterogeneous catalyst plays an important role in the determination of conformation of the resulting product. In this connection, it is interesting to observe the infrared dichroism arisen from the molecular orientation in the thin crystals of the Schiff base compounds formed on a palladium metal surface, because the molecular orientation of the intermediate may be deduced from the orientation of ethyl 2-hydroxyimino-3-oxo-3-phenylpropionate in thin films formed on the Pd surfaces, which can be determined by the high-sensitivity reflection technique.

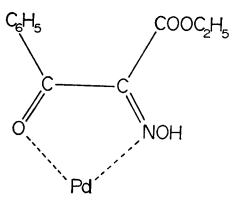



Fig. 1. Intermediate complex model.[10]

## Experimental

The infrared spectra were taken by means of a JASCO IR-G grating spectrophotometer with an assembly of JASCO model PR-41 for double beam reflection. The sample of ethyl 2-hydroxyimino-3-oxo-3-phenylpropionate was prepared according to the method given in literature.[11] Pd plates (99.9% in purity) were used as substrate. To obtain high reflectivity, the Pd plate was polished with silicon carbide and chromium oxide to its maximum flatness. After treating with 20% NaOH aqueous solution at 80 °C, the Pd plate was subjected to ultrasonic cleaning for *ca.* 30 min in distilled water to remove remaining alkali and air dried. The Pd plate was then immersed into a 0.5% ethanol solution of the Schiff base. After standing for 24 h or more at 5 °C, the Pd plate was taken out of the solution, and was dried in air. Thin films of the compound were formed on the plates upon evaporation of solvent. Unstable amorphous or stable crystal films were obtained depending upon the quantity of the solution remaining on the Pd surfaces, as will be described below.

## Results and Discussion

*Assignments of vibrational bands.* Since no infrared spectrum of ethyl 2-hydroxyimino-3-oxo-3-phenylpropionate, $C_6H_5COC(NOH)COOC_2H_5$ (abbreviated as EHOP) has appeared in literature, the infrared absorption bands of this compound must be assigned before the orientation of its molecule will be discussed. The assignment of the infrared bands of EHOP was made principally on the basis of comparison with the spectra of closely related compounds, $C_6H_5COC(NOH)COOCH_2C_6H_5$ (BHOP) and $CH_3COC(NOH)COOCH_2C_6H_5$ (BHOB), and their O-deuterated species.

Figure 2 shows the absorption spectrum of EHOP, obtained in KBr pellet in the range between 4000 and 600 $cm^{-1}$. The moderately strong band with maximum at 3310 $cm^{-1}$, which shifted on deuteration to 2445 $cm^{-1}$, can be assigned to the OH stretching vibration. A sharp band due to the free OH group was observed at 3555 and 3530 $cm^{-1}$ in dilute $CCl_4$ and $CS_2$ solutions, respectively, and no band could be observed around 3310 $cm^{-1}$. The 3310 $cm^{-1}$ band observed in the solid state is, therefore, certainly attributable to the intermolecular hydrogen bonded OH group. The strong bands at 1735 and 1675 $cm^{-1}$ are assigned to the carbonyl stretching of ester and ketone, respectively.[12] Similar bands are observed in the solid state spectra of BHOP (1728 and 1682 $cm^{-1}$) and BHOB (1740 sh, 1732, and 1690 $cm^{-1}$).

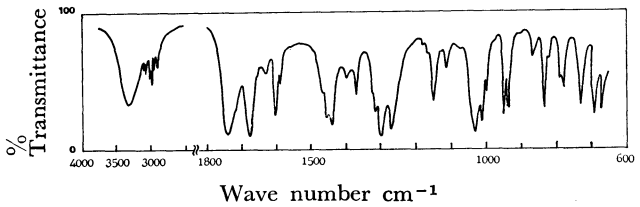



Fig. 2. Infrared absorption spectrum of $C_6H_5COC(NOH)COOC_2H_5$(KBr).

In most oximes, the C=N stretching band[13] appears at 1618—1660 $cm^{-1}$. This band corresponds to the weak one observed at 1627 $cm^{-1}$ in this molecule. The weakness and low frequency of the C=N stretching band are probably due to the conjugations between the adjacent C=O groups.[14] The 1438 $cm^{-1}$ band, which shifted to 1094 $cm^{-1}$ on deuteration, is assigned to the OH in-plane deformation vibration.

In the region between 1300 and 1000 $cm^{-1}$, two intense bands are expected to appear,[12] *viz.*, the vibrations of ester C–O–C antisymmetric stretching and phenyl-carbonyl C–C stretching vibrations. EHOP does really give two strong bands, at 1298 (vs) and 1272 $cm^{-1}$ (s), as is shown in Fig. 2. The 1298 $cm^{-1}$ band disappeared on conversion of the ester group into $COO^-$ group, while the 1272 $cm^{-1}$ band remained unchanged. Therefore, the former band can be ascribed to the ester C–O–C antisymmetric stretching vibration and the latter to the phenyl–carbonyl C–C stretching vibration. This assignment is supported by the fact that BHOP also gives bands at similar frequencies, *i.e.*, at 1288 (vs) and 1273 (s), but BHOB shows only one band at 1240 $cm^{-1}$ (s) around 1300 $cm^{-1}$.

Table 1. Observed frequencies and assignments of EHOP

| Frequency ($cm^{-1}$) | Assignment |
|---|---|
| 3310 m | bonded OH str. (2445) |
| 1735 s | ester C=O str. |
| 1675 vs | ketone C=O str. |
| 1627 vw | C=N str. |
| 1597 m | phenyl ring |
| 1583 w | phenyl ring |
| 1452 sh | phenyl ring |
| 1448 m | $CH_3$ asym. def. |
| 1438 m | OH in-plane def. (1094) |
| 1370 w | $CH_3$ sym. def. |
| 1322 sh | $CH_2$ def. |
| 1313 m | $CH_2$ def. |
| 1298 vs | ester C–O–C anti-sym. str. |
| 1272 s | phenyl-carbonyl C–C str. |
| 947 m | OH out-of-plane def. (635) |
| 935 m | NO str. (930) |
| 693 m | phenyl C–H out-of-plane def. |

Values in parentheses correspond to the peaks of O-deuterated compound.

Oximes give bands, in a range of 1000—900 $cm^{-1}$ due to the NO stretching and OH out-of-plane deformation vibrations.[15] Because the band at 947 $cm^{-1}$ decreased in intensity on partial deuteration and at the same time a new band appeared at 635 $cm^{-1}$, the 947 $cm^{-1}$ band can be assigned to the OH out-of-plane deformation. The band at 935 $cm^{-1}$ which shifted slightly toward lower frequency on deuteration may be attributed to the NO stretching, because the vibration is expected to be somewhat coupled with the OH in-plane deformation vibration. The assignments thus obtained are collected in Table 1.

*Molecular Conformation.* When EHOP was dissolved in $CCl_4$, the ester carbonyl band split into a doublet at 1752 and 1726 $cm^{-1}$. The doublet was also observed with BHOP at 1752 and 1725 $cm^{-1}$ (see Fig. 3). Since the molecules are essentially free in the above mentioned dilute solutions, the observed bands at 1752 and 1726 $cm^{-1}$ can be assigned to the nonbonded carbonyl group of ester.

It is well known that, in $\alpha,\beta$-unsaturated carbonyl compounds, the carbonyl stretching band often splits in dilute solution into two bands corresponding to two rotational isomers. An example is seen in benzalacetone in $CCl_4$ solution.[16] Cromwell *et al.* ascribed to the band appearing at a high frequency to the *s-cis* form and the low frequency one to the *s-trans* form. By analogy, we assigned the 1752 and 1726 $cm^{-1}$ bands mentioned above to the *s-cis* and *s-trans*, respectively (see Fig. 4). In the case of BHOB, solid state spectrum showed a doublet at 1740 (sh) and 1732 $cm^{-1}$, both ascribed to the carbonyl stretching of ester, while no doublet was observed in $CCl_4$ dilute solution but the ester carbonyl stretching band appeared at 1754 $cm^{-1}$. From its position, the 1754 $cm^{-1}$ band is to be attributed

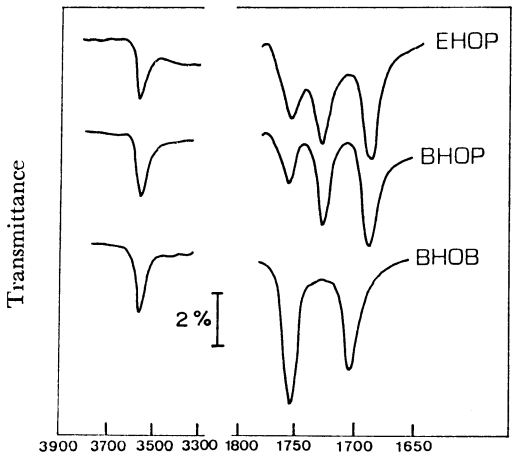



Fig. 3. Infrared spectra of ethyl 2-hydroxyimino-3-oxo-3-phenylpropionate (EHOP) and related compounds in $1\times10^{-3}$ molal solutions in $CCl_4$ (0.5 mm layer): EHOP = $C_6H_5COC(NOH)COOC_2H_5$; BHOP = $C_6H_5COC(NOH)COOCH_2C_6H_5$; BHOB = $CH_3COC(NOH)COOCH_2C_6H_5$.

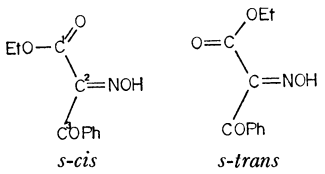



Fig. 4. Rotational isomers around the $C^1$–$C^2$ bond.

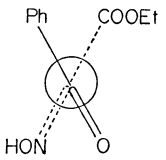



Fig. 5. Molecular conformation of EHOP, as viewed along the $C^2$–$C^3$ bond.

to the *s-cis* conformer. By structural analogy, the 1752 $cm^{-1}$ (*s-cis*) band observed in the solution spectrum of EHOP probably corresponds to the 1735 $cm^{-1}$ band observed in the solid phase, suggesting that the ester C=O (*s-cis*) group participates in the OH···O=C bond in the solid.

The rotational isomerism around the $C^2$–$C^3$ single bond is also possible in EHOP. However, the spectrum showed no doublet band of the ketone carbonyl stretching: the ketone C=O stretching band was observed at 1685 $cm^{-1}$ in $CCl_4$ solution, slightly shifted toward higher wave numbers than the corresponding band in the solid phase.[16] This fact indicates that EHOP molecule exists in only one form around the $C^2$–$C^3$ bond. Taking into account the steric hindrance and electrostatic effects in this molecule, the most probable conformation of this molecule can be obtained as drawn in Fig. 5. In this figure the carbonyl bond adjacent to the phenyl group is assumed to be coplanar with the phenyl ring because of the predicted strong conjugation between them. The C=N bond and the ketone C=O bond are located at the non-planer *s-cis*

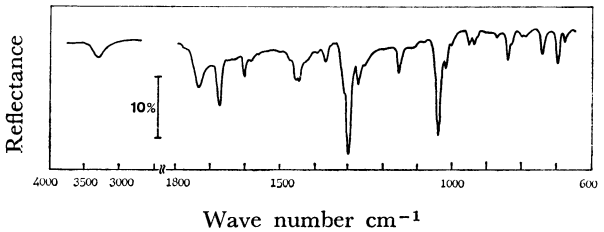



Fig. 6. High-sensitivity reflection spectrum of the thin film **A**.

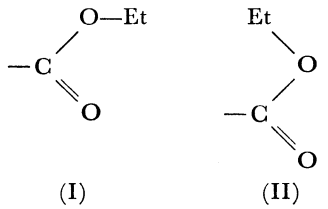
for the reason that the fixation of these groups at the *s-trans* position would result in the sever repulsion a between lone-pair electrons of oxygen atom of the ketone carbonyl and those of ethoxy group. This conformation can be strongly supported by the infrared dichroisms of oriented EHOP films, as will be described below. The rotation of the ethyl group around the ester C–O bond will be mentioned later.

*Reflection Spectra and Orientations.* The evaporation of solvent from the thin liquid film remaining on Pd resulted in a continuous thin crystal film **A**. On the other hand, when the liquid film was thick, an amorphous solid film was formed which was unstable and crystallized into islands. The resulting film is called as **B**.

The high-sensitivity reflection spectrum of the film **A** is shown in Fig. 6. The absorption bands of the film appear at almost 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 the spectrum gave no new band in Fig. 6 and the possibility of decomposition during the treatment can be ruled out. As mentioned above, the spectrum obtained by means of the high-sensitivity reflection method is regarded as a polarized spectrum, because it results from the interaction of molecular vibration with oscillating electric field polarized normal to the plane of reflection or the Pd mirror surface. Therefore, the observed changes in band intensity is obviously ascribed to the molecular orientation in crystals.[3,4,17] Since the relative intensities of the observed bands depends on the orientation of the vibrational transition moments, the molecular orientation can be determined, based on the relative intensities and the vibrational assignments as mentioned above.

When the molecular and crystal structure of this compound is known, the orientation of all the groups of the molecule may be determined. Unfortunately, however, X-ray diffraction data is not available and the orientation will be discussed based on the molecular conformation assumed above. Because the electric vector of infrared radiation in the vicinity of Pd surface is practically normal to that surface, absorption bands must have the maximum intensity, when the vibrating electric vector is perpendicular to the palladium surface. The most noteworthy feature in Fig. 6, is the enhanced intensity of the band due to the ester C–O–C antisymmetric stretching and weakness of the ester C=O stretching. These facts can be used in determining the probable conformation of the ester group from

the two possible forms:




(I) (II)

The directions of the transition moments of the C=O stretching and the C–O–C antisymmetric stretching are approximately normal with each other in the conformation (I) and is parallel in the conformation (II). The relative intensities of the two bands mentioned above lead to the deduction that the conformation (I) is likely; this conformation agrees well with that known for normal acetate esters.[18] The high dichroic ratio obtained for the ester C=O stretching and the C–O–C antisymmetric stretching bands further shows that the ester group lies in a plane as a whole and that its plane is normal to the metal surface. The enhanced intensity of the $\nu_{as}$ (C–O–C) band indicates that the C–C axis of the ester probably lies perpendicular to the metal surface, whereas the C=O bond is nearly parallel to the surface. The carbonyl stretching band of ketone appears as a moderately intense band, indicating that this bond probably lies obliquely oriented to the metal surface. The fact that the band at 1275 $cm^{-1}$, due to the phenyl–carbonyl C–C stretching is much decreased in intensity, indicates that the C–C bond is largely tilted from the direction normal to the palladium substrate. No information is available from C=N stretching band as it is too weak in the thin film as well as in the bulk state spectrum to provide any useful information.

Other noticeable features in the spectrum of Fig. 6 are much decreased intensities of the bands at 947 and 935 $cm^{-1}$, arising from the OH out-of-plane deformation and NO stretching vibrations, respectively. The former gives information about the hydrogen bond as well as the OH alignment with respect to the substrate and will be noted later, while the latter indicates that the NO bond is oriented nearly parallel to the substrate surface. Based on the discussion mentioned above, the most probable molecular orientation in thin EHOP film on the Pd substrate can be obtained as shown in Fig. 7.

Figure 8 shows the high-sensitivity reflection spectrum of the thin crystal film **B**. Since the spectrum obtained

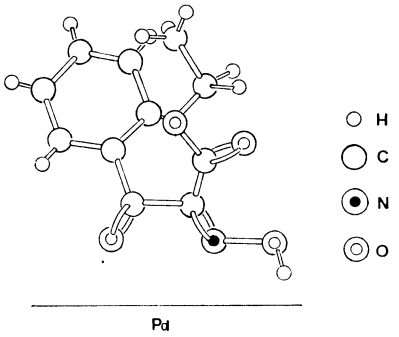



Fig. 7. Molecular orientation in the thin crystal **A**.

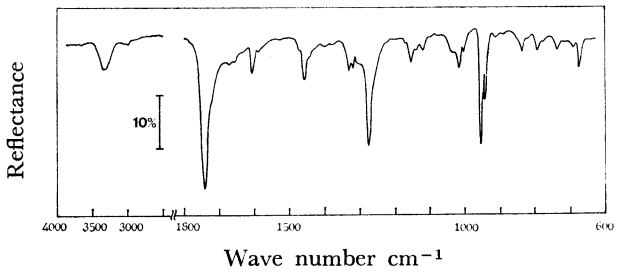



Fig. 8. High-sensitivity reflection spectrum of the thin film **B**.

just after evaporation of solvent ethanol was extremely weak and broad, this film may be regarded as amorphous. Although the relative intensity of the bands roughly agreed with that of the film **A**, the film was unstable and the crystallization soon occurred. After the crystallization, the absorption bands were much enhanced in intensity but the relative intensities of the bands differed remarkably from that in bulk spectrum of Fig. 2. The spectrum of the film **B** obtained by superposing the high-sensitivity reflection spectrum on the transmission one agrees well with the bulk spectrum, as will be described below. This fact clearly shows that the film was composed almost exclusively of EHOP and the change in relative intensity arose from the molecular orientation.

Most remarkable in Fig. 8 is the enhanced intensity of the band due to the ester C=O stretching and the extreme weakness of the ketone C=O stretching band. These facts indicate that the ester C=O bond is probably oriented perpendicular to the Pd surface, while the ketone C=O bond is not so.

The transmission measurement was carried out on film **B** formed on the sufficiently thin film of Pd deposited in a vacuum on a KBr window. The transmittance of the substrate plate used was about 30% throughout the examined frequency range. An ethyl alcohol solution of EHOP was put on the substrate surface. After evaporation of the solvent, the molecules soon crystallized in the same fashion mentioned above. To compensate the transmission loss of the substrate, a substrate prepared in the same procedure was placed in the reference beam. The signals were expanded by a factor of 5 on the recorder. The transmission spectrum obtained is shown in Fig. 9. Remarkable differences in band intensity can be seen when this spectrum is compared with that obtained by reflection method.

The spectrum obtained by superposing the reflection spectrum of the thin film on the transmission one is in good agreement with the spectrum of bulk sample

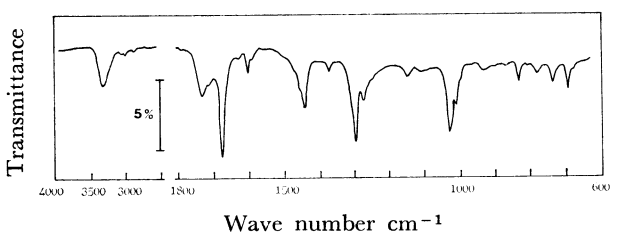



Fig. 9. Transmission spectrum of the thin film **B**.

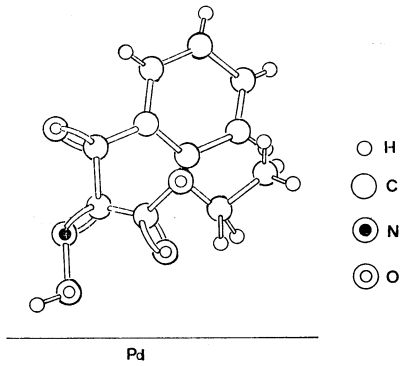



Fig. 10. Molecular orientation in the thin crystal **B**.

(Fig. 2), except slight shifts in band position caused by the difference in the measuring method. As can be seen in Fig. 9, the ketone carbonyl stretching and the ester C–O–C antisymmetric stretching bands are strongest in intensity, whereas the ester carbonyl stretching, the phenyl–carbonyl C–C stretching, and the NO stretching bands are weak. Because the electric field of incident radiation is parallel to the substrate surface and is orthogonal to that in the reflection method, the bands having enhanced intensity in the reflection spectrum must be weak in intensity in the transmission one, if the molecules are oriented. This is the case for the spectrum in Fig. 8 and that in Fig. 9, and the molecular orientation, mentioned above, is confirmed. The intensity of the OH out-of-plane deformation band is extremely weak in the spectrum of Fig. 9, indicating that the transition moment of the OH out-of-plane deformation vibration lies normal to the substrate surface. The transition moment of the OH in-plane deformation is in the plane of the OH···O unit and so stronger in intensity than the OH out-of-plane deformation in the transmission spectrum. These facts indicate that the OH···O plane in crystal **B** is lying nearly parallel to the Pd surface. Because the phenyl–carbonyl C–C stretching is observed as a moderately strong band in Fig. 8, the molecular orientation in the film **B** can be deduced as shown in Fig. 10. In accord with this orientation, NO stretching appears as an enhanced band as can be seen in Fig. 8.

In discussing the mechanism of the catalytic asymmetric hydrogenation, the direct determination of the orientation of species strongly adsorbed on the catalytic surface is quite desirable. However, the signal from such the species in a trace is too weak to provide any available information. It should be mentioned here that, according to recent experiments,[7] the orientation of molecules in a thin film is strongly governed by the orientation of the species which are adsorbed strongly on the substrate surface and which subsequently acts as the nuclei for crystal overgrowth. The molecular orientation thus taken place is generally maintained as far as the film is very thin. The orientations of the EHOP molecule in the thin film **A** may, therefore, correspond to that of species strongly adsorbed on the palladium surface. It must be mentioned that the molecular orientation in the extremely thin film **A** is essentially the same as the model proposed by Harada *et al.*[9] (see Fig. 1). Since the strain caused by crystallization may result in the change of orientation, and the molecular orientation in the film **B**, probably, does not correspond to that of the species strongly adsorbed on palladium.

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