CHEMISTRY LETTERS, pp. 843-846, 1985. © 1985 The Chemical Society of Japan

THE ADSORPTION OF ETHYL ACETOACETATE ON NICKEL MODIFIED WITH D-α-ALANINE STUDIED BY POLARIZATION MODULATION IR SPECTROSCOPY

Aritada HATTA,* Takashi KOBAYASHI, Toshimasa WADAYAMA, and
Wataru SUËTAKA
Laboratory of Interface Science of Metals, Faculty of Engineering,
Tohoku University, Aramaki Aoba, Sendai 980

Polarization modulation infrared reflection spectroscopy has been used to obtain the absorption spectrum of ethyl acetoacetate (EAA) adsorbed on Ni modified with optically active D-α-alanine. The obtained spectrum can be explained in terms of a particular orientation of EAA on the modified Ni surface. The adsorption of EAA exerts some influence upon the spectrum of D-α-alanine.

Infrared reflection absorption spectroscopy (IRRAS)$^{1)}$ is a valuable tool for the study of real metal surfaces, because it permits in-situ observation of surface species in relatively high pressure gaseous environments, in contrast to high-resolution electron energy loss spectroscopy. Recently, the sensitivity of IRRAS has been greatly improved by the use of polarization modulation(PM) method. PM-IRRAS provides not only a sensitive means for the detection of adsorbed molecules on metal surfaces,$^{2)}$ but also a unique tool for detecting weakly adsorbed species and metastable reaction intermediates, which persist only in the presence of gaseous molecules at room and elevated temperatures.$^{3)}$

The hydrogenation of methyl acetoacetate over Raney nickel modified with optically active hydroxy or amino acids results in either of the optical isomers of methyl-β-hydroxybutyrate, depending upon the optical activity of the compound used as the modifying reagent.$^{4)}$ Though the detailed mechanism is still unknown, an important observation is that only optically active acids in which a hydroxy or amino group is attached to the asymmetric carbon atom are active for such an asymmetric reaction. Therefore, the geometry of the modifying reagent adsorbed on the Raney nickel catalyst, as well as the interaction of methyl acetoacetate with the modified surface, would play important roles in the determination of the configuration of the reduction product. To shed some light on the unresolved mechanism, we previously investigated infrared dichroism arising from the preferable orientation of some modifying molecules present on Ni by means of a conventional IRRAS method.$^{5,6)}$ However, no direct information on the nature of methyl acetoacetate interacting with modifiers has yet been obtained. In the present work, we applied the PM-IRRAS method$^{7)}$ to investigate ethyl acetoacetate (EAA) adsorbed on Ni modified with D-α-alanine.

An electrolytic Ni plate (99.9% purity) was used as a substrate. EAA was

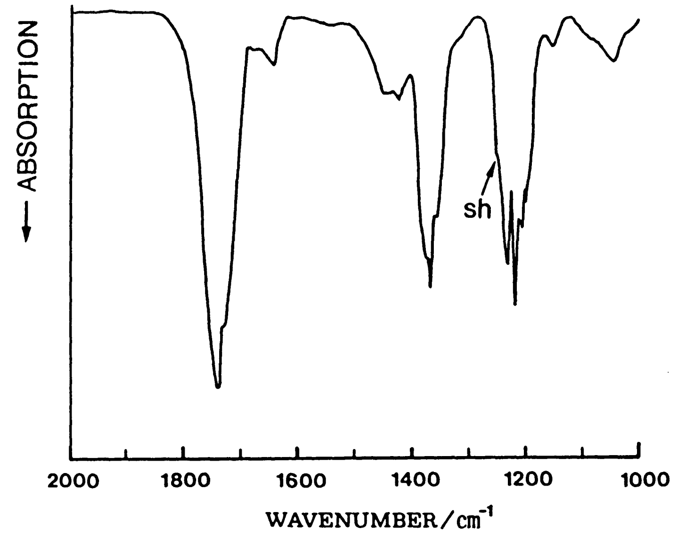

Fig. 1. Transmission spectrum of ethyl acetoacetate vaporized rapidly.

allowed to vaporize rapidly from the liquid into an IR cell pre-evacuated at 5×10^{-4} Torr at room temperature. EAA consists of a mixture of enolic and ketonic forms in the vapor phase. Figure 1 shows the transmission spectrum obtained from rapidly evaporated EAA. The result shows close resemblance to the spectrum of liquid EAA in the keto form, except for the rotational band contours appearing in Fig. 1. Overlapping bands of the carbonyl stretching vibrations of the ester and ketone groups are observed at about 1740 cm^{-1}. The moderately strong band centered at 1365 cm^{-1} is assigned to the symmetric deformation of the CH_3 group attached to the ketone carbonyl group.[8)] The band centered at 1220 cm^{-1} can be assigned to the C-O-C antisymmetric stretching, whereas the 1040 cm^{-1} band may stem from the C-O-C symmetric stretching. All the bands mentioned above are ascribed to the keto form of EAA. On the other hand, the bands at 1670, 1640, and 1250 cm^{-1}(sh), which can be assigned to the enol form, are observed only weakly. It is thus concluded that the EAA gas consists mostly of the keto form, when vaporized rapidly.

Figure 2 is the PM-IRRAS spectrum of a Ni surface obtained after 1 Torr of EAA admission. As can be seen in Fig. 2, the spectrum exhibits only two strong bands at 1747 and 1238 cm^{-1}, attributable to the keto conformer; the former arises probably from the ester C=O stretching and the latter from the ester C-O-C antisymmetric stretching. The intensity of the band due to the C-O-C antisymmetric stretching relative to that of the C=O stretching increases in changing the state from vapor to adsorbed. The wavelength region from 6.5 to 7.7 μm, where no band could be observed, is omitted in Fig. 2. It should be noted here that absorption corresponding to the CH_3 symmetric deformation appearing in the vapor phase spectrum could not be observed for the surface species. These spectral changes may

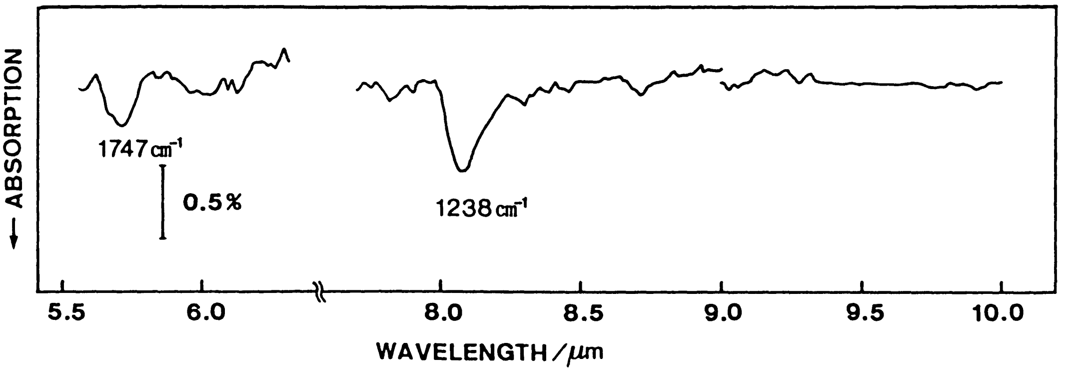

Fig. 2. Polarization modulation IRRAS spectrum of ethyl acetoacetate adsorbed on a nickel metal surface at room temperature.

be interpreted in terms of a molecular orientation of the EAA adsorbed on the Ni surface. Since the absorption bands of the adsorbate disappeared upon pumping off the vapor at room temperature, interactions between the adsorbed species and the Ni surface should be weak.

Figure 3 shows PM-IRRAS spectra from a Ni surface modified with D-α-alanine in its aqueous solution at 20 °C.$^{6)}$ Spectrum A is obtained from a modified nickel surface in vacuum. The prominent feature at 1610 cm^{-1} is ascribed to vibrations of the NH_3^+ degenerate deformation overlapped with the CO_2^- antisymmetric stretching of D-α-alanine$^{6)}$; in addition the spectrum shows a number of weak bands due to D-α-alanine. The curve B is the spectrum of the modified Ni surface recorded after introduction of 1 Torr EAA into the cell. The subtraction of spectrum A from B yields spectrum C, after a vertical enlargement by a factor of two.

The difference spectrum thus obtained gives information about the adsorbed EAA on the modified Ni surface. The spectrum exhibits a strong band at 1240 cm^{-1}, at essentially the same frequency as in Fig. 2, and hence ascribed to the ester C-O-C antisymmetric stretching vibration. However, the carbonyl stretching band cannot be located in the spectrum C. This spectral change may also be attributed to a preferable orientation of EAA due to the interactions with D-α-alanine.

The absorption peak at 1240 cm^{-1} disappeared upon evacuation and the spectrum B reverted to the original spectrum A. The most striking feature in C is the large negative band centered at 1618 cm^{-1}, which has probably arisen from the decrease in absorption intensity of the NH_3^+ degenerate deformation or the CO_2^- antisymmetric stretching band of D-α-alanine. Since no other negative absorption is ob-

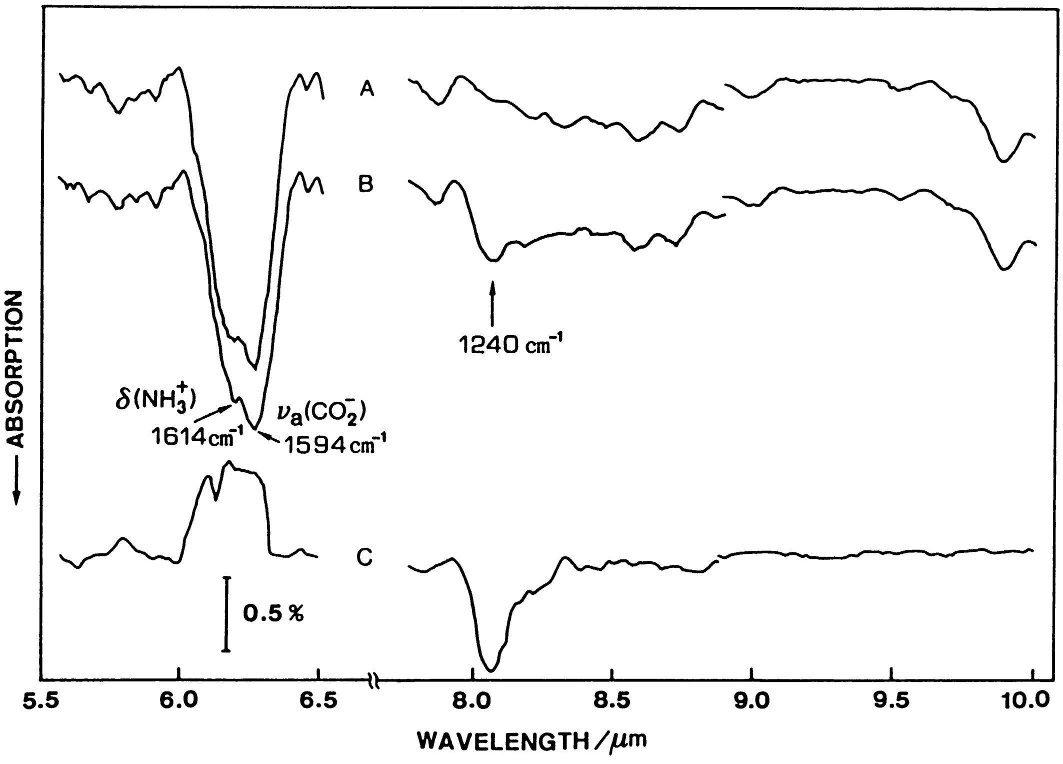

Fig. 3. PM-IRRAS spectra of (A) D-α-alanine modified Ni surface, (B) after adsorption of ethyl acetoacetate, (C) difference spectrum; (B)-(A).

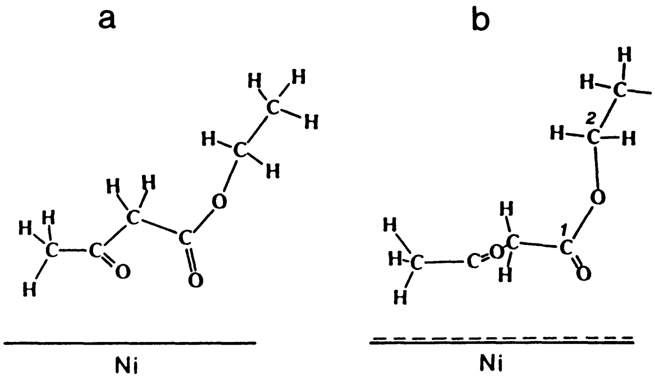

Fig. 4. Molecular orientation models of EAA on (a) bare Ni and (b) D-α-alanine modified Ni.

served in C, the spectral change may stem from an interaction between EAA and the CO_2^- (or NH_3^+) group of D-α-alanine.

In the IRRAS method only vibrational bands having oscillating dipole moments perpendicular to the metal surface should be observed. Taking this into account, molecular orientations of EAA adsorbed on the bare and D-α-alanine modified Ni surfaces can be drawn as depicted in Fig. 4. In drawing the models, an approximate molecular conformation was assumed for EAA by considering the steric hindrance and electrostatic effects to be involved in the molecule. In Fig. 4(a), the ketone carbonyl is aligned nearly parallel to the Ni surface while the ester carbonyl lies obliquely to that surface. In Fig. 4(b), the ester carbonyl is largely tilted from the direction normal to the metal surface, whereas the $C_1 \cdots C_2$ axis of the ester group is aligned nearly vertical to the surface. Figure 4 indicates that the modifier molecule exerts an influence upon the molecular orientation of EAA, and the intermolecular forces acting between D-α-alanine and EAA molecules may be important in determining the optical activity of the reduction product obtained by the asymmetric synthesis.[4] Thus far we have described the orientational behavior of EAA based on the keto conformer. However, the results of the present study do not exclude the participation of the enol conformer in the asymmetric hydrogenation reaction.[9]

This work was supported by Toray Science and Technology Grants and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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(Received April 11, 1985)