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METASTABLE CRYSTAL IN THIN FILMS OF MALEIC ACID ON METAL SURFACES

Koichi SUZUKI, Aritada HATTA, and Wataru SUËTAKA
Laboratory of Interface Science of Metals, Faculty of Engineering,
Tohoku University, Aramaki Aoba, Sendai 980

Infrared spectra of thin maleic acid films formed on metal surfaces by vacuum deposition showed that the crystal structure in the thin films changes depending upon the condition of the metal surface. The films grown on fresh surfaces had a metastable crystal structure, in which hydrogen bonds are weaker than in the ordinary crystal.

When an organic film is grown on a solid substrate, the structure of nucleus formed under the interaction of the substrate may persist in the film, provided its thickness is very small, even though the structure is unstable in the bulk state. In the present communication, we wish to report the formation of a metastable crystal found in the thin films of maleic acid on fresh metal surfaces.

A conventional belljar-type vacuum evaporation system was used for the preparation of thin maleic acid films and metal substrates. The latter was deposited on glass plates at pressures of 10^{-3}—10^{-4} torr. The purities of the used metals, Al, Cu, Fe, and Ni, were 99.99, 99.999, 99.5, and 99.9 %, respectively. Powdered maleic acid in a glass tube was heated nearly to the temperature of its melting point (130°C) and deposited on the metal substrate at room temperatures. The thickness of the deposited films was estimated to be in the range of 0.1 to 1μ.

Fig.2(A) shows the infrared high sensitivity reflection spectrum1) of the thin maleic acid on a fresh nickel surface. The infrared absorption spectrum in the bulk state is also shown in Fig.1. Fig.2(B) shows the spectrum of the film formed on a nickel surface, which was exposed to air before the deposition of the organic compound. The curves are displaced vertically for avoiding overlapping. The spectrum (B) agrees completely with that of the thin films formed on metal surfaces from solution2); all the absorption bands except those arisen from the out-of-plane deformation vibrations decrease remarkably in intensity, indicating the orientation of maleic acid molecules parallel to the metal surface.

The infrared anisotropy is also seen in the spectrum of Fig.2(A), which shows that the plane of molecule should be nearly parallel to the metal surface. The change in the position of bands, which can be seen in the region of 1680--1730 and 930--1000 cm^{-1}, however, can not be attributed to the molecular orientation. Maleic acid may be changed into fumaric acid or maleic anhydride on vacuum deposition. The absorption bands at 1730, 950, and 936 cm^{-1}, however, can be attributed to neither of these compounds. Furthermore, the spectrum of thin film changed with time, resulting in the spectrum of strongly orientated maleic acid crystal as will be stated below. It is quite unlikely, therefore, that the compound in the thin film on fresh nickel surface was fumaric acid or maleic anhydride.

Since the bands at 990 and 936 cm^{-1} shifted to 700 and 665 cm^{-1} respectively upon deuteration, these bands can be assigned to the O-H out-of-plane deformation vibrations. The band in the former region is considered to be arisen from C=O stretching vibration. Because in the maleic acid crystal the intra-

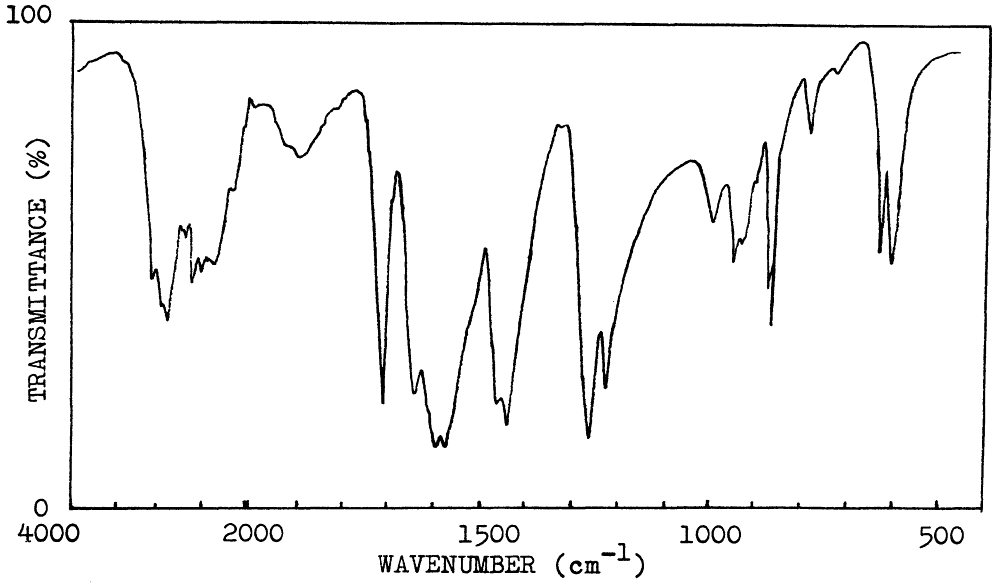

Fig.1 Infrared spectrum of maleic acid in powdered crystal (Nujol mull)

and inter-molecular hydrogen bonds are formed between C=O and O-H groups,3) the above mentioned change in band position indicates that the thin film on fresh metal surface probably contains a hydrogen bond system different from that in the bulk state.

The infrared spectrum of the thin film on fresh nickel surfaces changes with time as shown in Fig.2(A′) ; the bands at 1730 and 950 cm^{-1} decrease remarkably in intensity and new bands appear at 1700 and 990 cm^{-1}, which correspond to those in the bulk state. The change in the spectrum shows that the structure in the thin film on nickel surface is not stable and changes into that in the bulk state. The spectra of the thin films on fresh iron surfaces were in rough agreement with that on fresh nickel surfaces and changed with time into the spectra of strongly orientated maleic acid crystals.

Fig.3 shows the spectra of thin films on aluminum surface. The spectrum (A′),

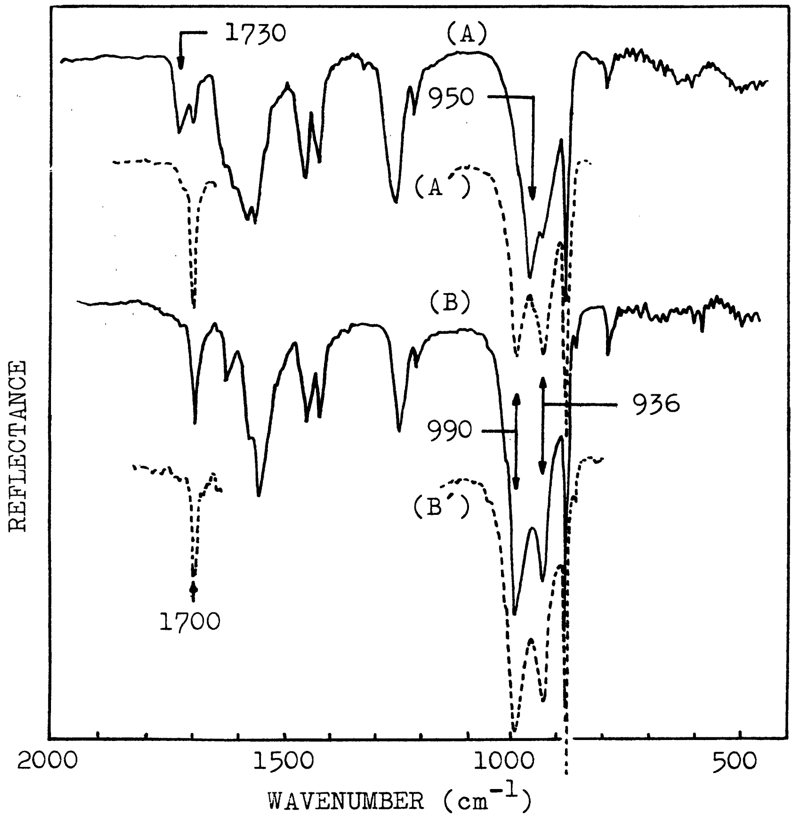

Fig.2 Infrared spectra of maleic acid thin film on nickel surface.
(A) : Film on the fresh surface; immediately after deposition
(A′) : idem ; 24hr after deposition
(B) : Film on the surface exposed to air ; immediately after deposition
(B′) : idem ; 24hr after deposition

in this figure, differs only slightly from the spectrum (A), showing that the crystal on fresh aluminum surface is fairly stable in contrast with the films on nickel or iron. The spectra of the films on copper surfaces resembled to those on aluminum surfaces.

The discussion about the active sites for nucleation and the stability change with substrate metal requires the information obtained with the surfaces cleaner than those used in the present work, and experiments at higher vacuum are planned.

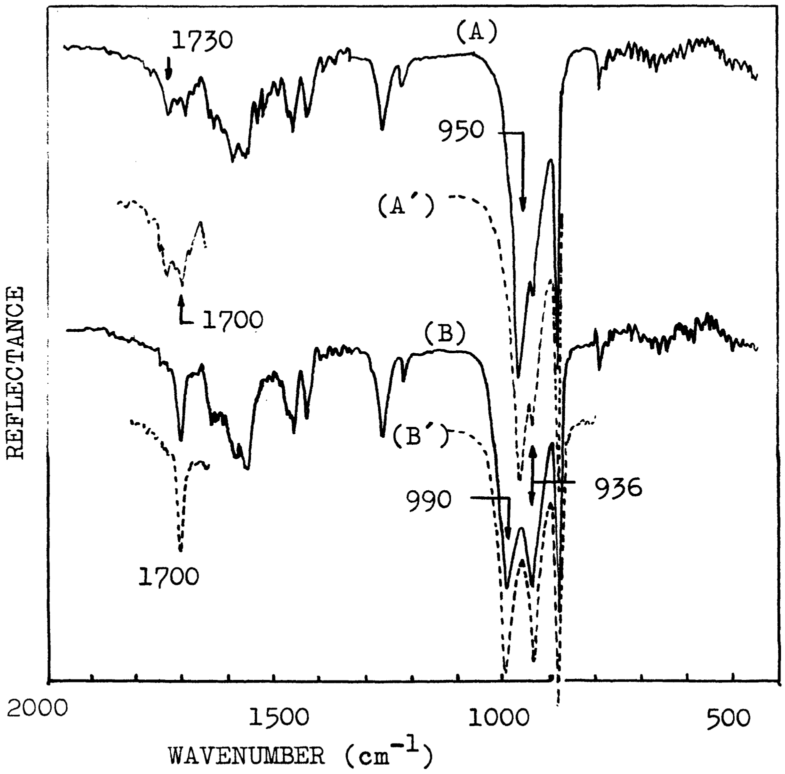

Fig.3 Infrared spectra of maleic acid thin film on aluminum surface. Notations as in Fig.2

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