Adsorption States and Modifier−Substrate Interactions on Pt(111) Relevant to the Enantioselective Hydrogenation of Alkyl Pyruvates in the Orito Reaction

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The asymmetric hydrogenation of α-ketoesters on chirally modified Pt catalysts, the Orito reaction, is the subject of intense current study.[1] The great challenge posed by the Orito reaction arises from the fact that mutually interactive roles for the metal surface, the α-ketoester, the modifier, the solvent, and hydrogen must be taken into account. Proposed reaction mechanisms are based largely on extensive data taken from catalysis runs and from models of the modifier−substrate interaction. More recently, in situ spectroscopic studies have yielded information obtained under true reaction conditions.[2] Simultaneously, there is an effort among several groups[3] to use surface spectroscopies to study the chemisorption of alkyl pyruvates and chiral modifiers. Reflectance FTIR spectroscopy (RAIRS) is a particularly useful technique for the study of issues related to the Orito reaction, in that it is sensitive to adsorbate orientation, to interadsorbate bonding, and to chemisorption-induced bond activation. This Communication presents RAIRS data for the adsorption of methyl pyruvate (MP) on both clean and (±)-1-(1-naphthyl)ethylamine (NEA)-modified Pt(111). Minder et al.[4] have shown that NEA (**3**) is competitive with cinchona alkaloids as a chiral modifier in the hydrogenation of ethyl pyruvate to ethyl lactate over Pt/Al₂O₃. The results presented herein show the presence of a majority enediolate state (**1**) on the clean surface. A perpendicularly adsorbed trans conformation state (**2**), populated at close to full-monolayer coverage on the clean surface, is rendered thermally stable in the presence of coadsorbed NEA. The stabilizing interaction is identified as hydrogen-bonding between the ester carbonyl of *trans*-MP and the NEA amine group (**4**).

Exposure of clean Pt(111) at 110 K to MP leads to **1**, displaying bands at 1543, 1452, and 1290 cm⁻¹ (Supporting Information).[5] Following saturation of the enediolate state at close to full-monolayer coverage, additional exposure at 110 K yields an adsorption state with a free carbonyl group characterized by a ν(CO) stretching frequency of 1742 cm⁻¹. This minority state also displays a ν(C−O$_{ester}$) band at 1307 cm⁻¹, but no out-of-plane ρ(O−CH₃) band. The latter, intense band grows in at 1150 cm⁻¹ following the completion of the monolayer (Supporting Information). The high-coverage minority state is thus assigned to an η^1-trans configuration (**2**), with the molecular plane oriented normal to the surface. The latter state is selectively removed on annealing to 190 K. Annealing to 230 K (data not shown) causes the loss of the enediolate features, consistent with the surface polymerization reaction reported by Bonello et al. for MP on clean Pt(111).[3i]

RAIRS spectra for the coadsorption of MP and NEA are displayed in Figure 1. Low-coverage NEA on Pt(111) (spectrum 1a) at 110 K yields a characteristic δ(NH₂) band at 1642 cm⁻¹. Adsorption of MP on the NEA exposed surface leads to the appearance (spectrum 1b) of enediolate bands at 1545 and 1290 cm⁻¹. Higher exposure to MP (spectrum 1c) populates the *trans*-MP state, as indicated by the free carbonyl band at 1742 cm⁻¹ and the ν(C−O$_{ester}$) shoulder at 1307 cm⁻¹. Two other *trans*-MP-induced changes should be noted in spectrum 1c: there are new bands at
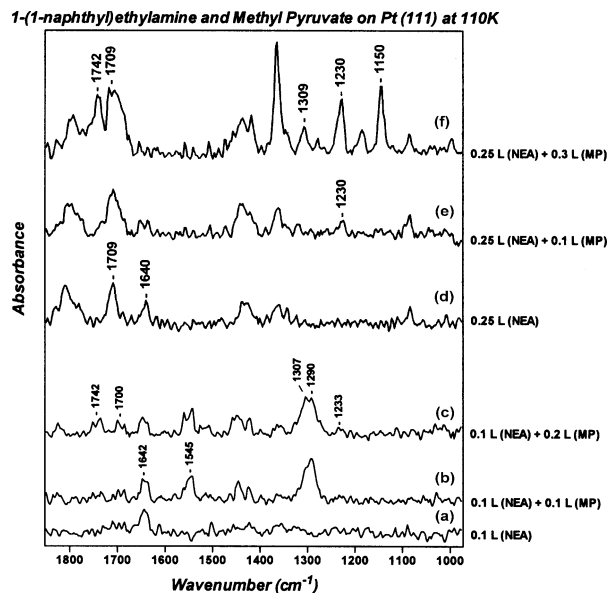

Figure 1. (a−c) RAIRS spectra for a 0.1 L (1 L = 1 × 10⁻⁶ Torr·sec) exposure of (±)-NEA on Pt(111) at 110 K, followed by consecutive exposures to methyl pyruvate. (d−f) RAIRS spectra for 0.25 L (±)-NEA followed by consecutive exposures to methyl pyruvate at 110 K.

1700 and 1233 cm⁻¹. The former is indicative of hydrogen-bond formation between a carbonyl group of **2** and the amine group of NEA. The band at 1700 cm⁻¹ may be attributed to the resultant blue-shift of the δ(NH₂) frequency and/or the red-shift of the ν(CO) frequency.[6] Higher initial exposure to NEA leads (spectrum 1d) to a band at 1709 cm⁻¹ due to NEA hydrogen-bond association. Exposure to MP leads to a clearly resolved band at 1230 cm⁻¹ (spectrum 1e). A comparison of spectra 1b and 1e shows that the higher precoverage of NEA inhibits the formation of **1**. Spectrum 1f shows the hydrogen-bonding interaction that occurs between high-coverage NEA and an overlayer of condensed MP. In particular, the interaction leads to the complete removal of the δ(NH₂) band at 1640 cm⁻¹ and the emergence of a strong ν(C−N) band at 1230 cm⁻¹. The enhancement of the ν(C−N) band in the presence of multilayer MP is attributed to a change in the orientation of the ethylamine function due to the carbonyl−amine hydrogen-bonding interaction. The similar effect observed in spectra 1c and 1e, leading to the observation of a weak band at ∼1230 cm⁻¹, is attributed to the formation of a 1:1 complex, **4**, between chemisorbed NEA and perpendicularly oriented chemisorbed *trans*-MP. Figure 2A shows that this hydrogen-bond adsorption complex remains stable to temperatures well above that for **2** on clean Pt(111). The carbonyl band due to **2** is present to 300 K (spectrum 2d) in the presence of NEA, whereas it is absent at 210 K (Figure 2B) on clean Pt (111). Spectrum 2e (Figure 2A) shows the destruction of the 1:1 complex by 350 K.
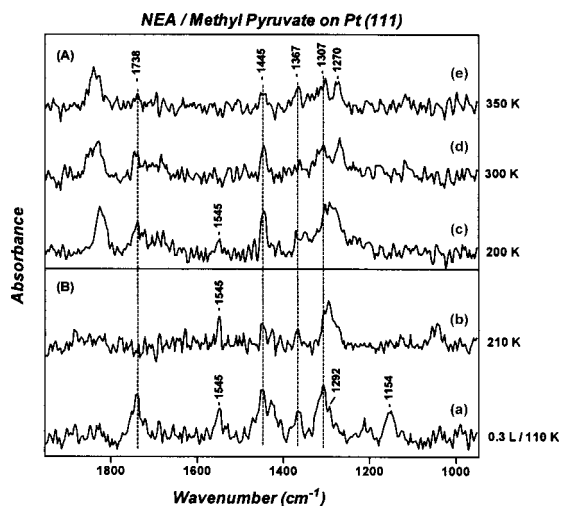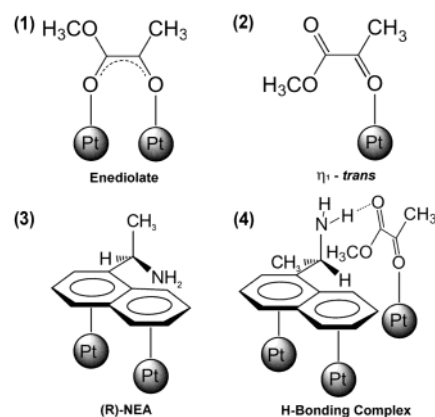
Figure 2. (A) RAIRS spectra, as a function of anneal temperature, for a coadsorbed layer formed by exposing clean Pt(111) to 0.3 L NEA at 110 K, followed by 0.5 L methyl pyruvate. (B) Spectra for methyl pyruvate on clean Pt(111) at 110 K and after an anneal to 210 K.

Scheme 1

As illustrated in Scheme 1, the hydrogen-bonding interaction between adsorbed *trans*-MP and NEA is assumed to occur via the ester carbonyl, given that the keto carbonyl forms the stronger chemisorption bond. Carbonyl–amine hydrogen-bond strengths can be as high as 7 kcal/mol,[7] a value similar to that of a carbonyl lone pair–surface interaction. It is proposed that the combined requirements of hydrogen-bond and chemisorption bond formation lead to a well-defined 1:1 complex, facilitated by the flexibility of the ethylamine group. STM images reported by Bonello et al.[3f] also provide direct support for a 1:1 adsorption complex. Sequential hydrogenation steps are then assumed to occur at the chemisorption-activated keto group, while the ester carbonyl–amine interaction serves to orient the pyruvate. A transient geometry in which the half-hydrogenated keto carbonyl group points toward the naphthalene anchor should be favored for two reasons. First, it permits a weak hydrogen-bond interaction with the ring, and second, it avoids steric repulsion between the methyl group and the ring. This energetic inequivalence provides the driving force for enantio-selection. The proposed mechanism differs, subtly, from all previous mechanisms for the Orito reaction. In common with most other mechanisms, it requires a nontemplate, 1:1 substrate–modifier interaction. The subtle difference is that this interaction is proposed to occur at the ester carbonyl in *trans*-MP oriented perpendicularly to the surface. We also wish to point out some observations relevant to an understanding of the modifier-induced rate-enhancement effect.[1a,b] Complex **4** serves to increase the surface concentration of *trans*-MP at the reaction temperature. A sufficient coverage of NEA inhibits formation of the enediolate state, **1**, thereby possibly blocking a competing racemic reaction pathway. The observation of a H-bond interaction between a condensed overlayer of MP and chemisorbed NEA (spectrum 1f) suggests that NEA can participate in capturing MP from the solution phase.

Supporting Information Available: Band assignments and RAIRS spectra of MP and NEA on clean Pt(111) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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