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Communication

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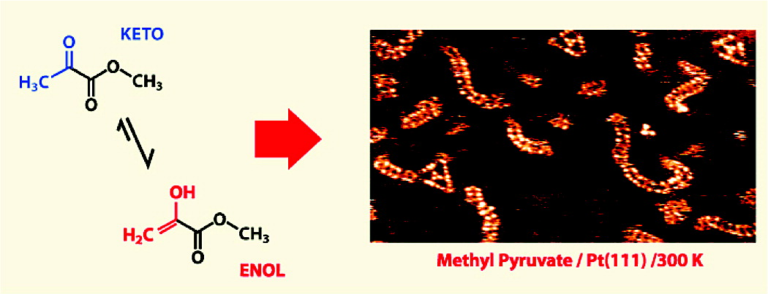
*J. Am. Chem. Soc.*, **2007**, 129 (38), 11668-11669• DOI: 10.1021/ja072638h • Publication Date (Web): 05 September 2007



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COMMUNICATIONS

# Keto-Enol Driven Assembly of Methyl Pyruvate on Pt(111)

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Chirally modified platinum catalysts may be used in the Orito reaction to stereoselectively hydrogenate a relatively wide range of activated ketones. It is recognized, however, that considerable tuning of reaction parameters such as choice of solvent, hydrogen pressure, catalyst pretreatment, and modifier concentration is required to achieve optimal ee for any specific modifier−substrate pair.[1] Furthermore, side reactions between adsorbed substrate molecules are believed to influence the performance of Orito catalysts.[2,3] Two effects of a reported surface polymerization reaction[2] of methyl pyruvate on Pt(111) have been discussed in the literature. One is the deactivation of the catalyst[2] and the second is its role in producing a measured rate-enhancement of the enantioselective reaction.[3]

In this Communication we show that methyl pyruvate undergoes CH bond scission at room temperature on clean Pt(111) leading to surface mediated enol formation and assembly into H-bonded superstructures. The self-assembly process can be severely inhibited by either keeping the Pt sample below the temperature for CH bond scission or, at room temperature, by applying a background pressure of $\sim 10^{-6}$ Torr $H_2$. The latter finding is in agreement with the results of studies by Bonello et al.[2] They, however, attributed superstructure formation, in the absence of background $H_2$, to an irreversible polymerization reaction. In contrast, the thermal desorption (TPD), reflectance absorbance infrared (RAIRS), and scanning tunneling microscopy (STM) data presented herein suggest that the superstructures are due to enol assembly, an easily reversible interaction.

Confirmation of CH bond scission in the acetyl moiety of methyl pyruvate below room temperature was obtained by performing TPD measurements on $CH_3COCOOCH_3$ (MP) and $CH_3COCOOCD_3$ (MPD). As shown in Figure 1, the leading edge for $H_2$ desorption is at ~290 K, whereas $D_2$ desorption only begins above 350 K. The $H_2$ desorption trace is consistent with reported data for the recombinative desorption of $H_2$ from Pt(111)[4] and is also in good agreement with literature data for methyl-group activation on Pt(111).[5] RAIRS spectra for saturation coverage of methyl pyruvate on Pt(111) at 300 K (Figure 2A) display a band at 1594 $cm^{-1}$, characteristic of the mixed $\nu(C{=}C)$ mode of an enol (Supporting Information).[6] The intensity of the band indicates that the CC bond is tilted with respect to the surface plane. The $\nu(C{=}C)$ band is not present on exposure alone at 215 K (2B) nor at 300 K under $\sim 10^{-6}$ Torr $H_2$ (2C). We propose that on clean Pt(111) at room temperature, $CH_3$ activation initiates enol formation and that proton transfer occurs via $H_{ads}$ in a surface-mediated process.

The conclusions based on the TPD and RAIRS data are supported by the results of STM measurements (Figure 3). Images recorded for moderate coverages of methyl pyruvate on clean Pt(111) at room temperature show both bimolecular chains and triangular structures (Figure 3A,B). At higher coverages, only chains are observed (Supporting Information). Images taken at intervals of 10 min show that the chains are mobile and that segments can detach from a given chain and randomly attach to other chains, indicating that superstructure formation is readily reversible at room temperature. High-resolution images of the molecules at the center of the triangular structures (Figure 3C) reveal an assembly of three "bowling pin" shaped protrusions of approximately the dimension of methyl pyruvate. In light of the RAIRS data, the individual bowling pin protrusions are attributed to the enol tautomer of methyl pyruvate.

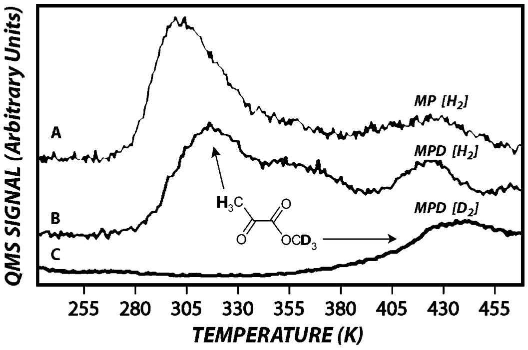

***Figure 1.*** (A) $H_2$ desorption spectrum for a monolayer of methyl pyruvate (MP) on Pt(111); (B and C) $H_2$ and $D_2$ desorption spectra for a monolayer of $d_3$-methyl pyruvate (MPD) on Pt(111).

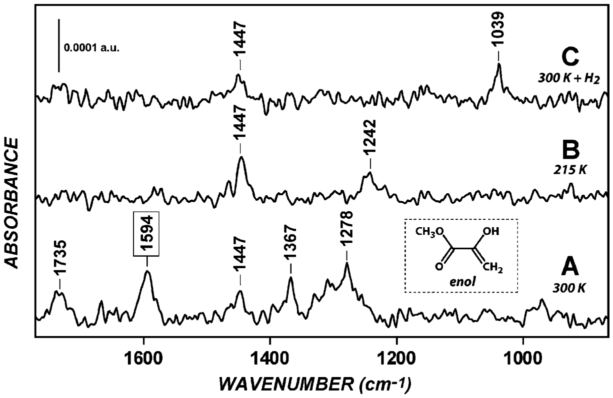

***Figure 2.*** RAIRS spectra of methyl pyruvate on Pt(111): (A) saturation exposure at room temperature; (B) monolayer at 215 K; (C) saturation exposure at room temperature in the presence of approximately $10^{-6}$ Torr $H_2$.

The enol form presents both H-bond acceptor (carbonyl/OH) and donor (OH) groups. Hence, a number of H-bonding interactions could account for self-assembly into the triangular (Figure 3C) and chain (Figure 3D) superstructures. STM data taken on exposure to methyl pyruvate at 150 K (Supporting Information) show no evidence for self-assembly into chains or triangles. This is attributed to the absence of the CH bond scission step required for surface mediated keto-enol tautomerization. The absence of chain and triangle formation at room temperature in the presence $\sim 10^{-6}$ Torr $H_2$ (Supporting Information) is attributed to the inhibition of the CH scission step[2b] and to hydrogenation of the ketoester. The

10.1021/ja072638h CCC: $37.00

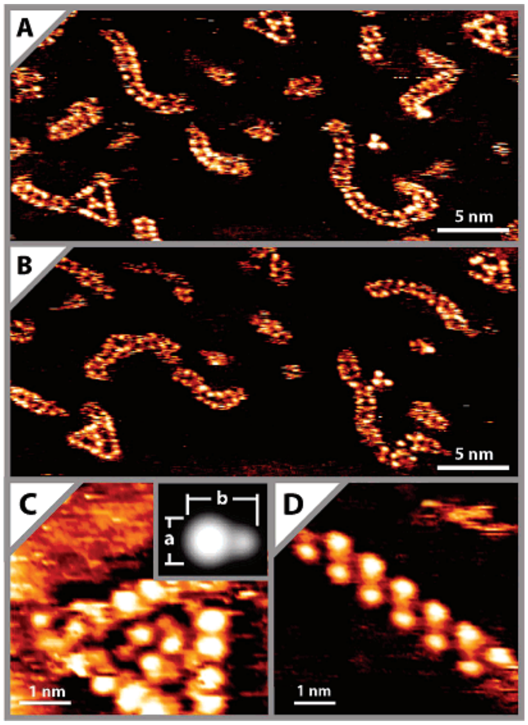

***Figure 3.*** Room-temperature STM data for methyl pyruvate on Pt(111): (A, B) images taken at 10 min intervals; (C) high-resolution image of a triangular structure. The insert illustrates the dimensions of a single structure within the triangle. ($a$ = 5 nm, $b$ = 8 nm). (D) High-resolution image of a chain structure. Tunneling conditions: voltage = −1 V; current = 1 nA.

present results showing reversible enol clustering rather than polymerization are consistent with the catalysis literature. The hydrogenation process on Pt, below 70% conversion, can be cycled for many periods without any loss of either enantiomeric excess or activity, indicating that releasing the $H_2$ pressure does not poison the catalyst irreversibly.[7]

Jeffery et al.[8] reported DFT calculations showing that enol and enolate forms of acetone on Pt(111) are more stable than either $\eta^1$ or $\eta^2$-adsorption states. These authors and Jenkins et al.[3c] noted that the enol form of $\alpha$-ketoesters might play a role in the asymmetric hydrogenation on cinchona-modified Pt. The surface science data presented above suggest that under hydrogen-poor conditions the enol form may indeed play a role. Hydrogen-poor conditions can arise in catalysis runs beause of mass transport effects even in the presence of high-hydrogen pressures.[9]

Enol formation could have a number of effects on the ee. First, enol clustering competes with the formation of modifier-substrate complexes and it lowers the surface diffusion rate of the substrate. Second, as outlined by Lavoie et al.,[10] a cinchonidine-enol complex would favor (*S*)-product formation in contrast to the (*R*)-product formed from cinchonidine-ketoester complexes. The relative rates of hydrogenation of enol and keto forms, at nonmodified sites, would also influence the ee. These factors may contribute to the strong dependence on $H_2$ pressure at low pressures that is observed in some cases. For example, the ee for ethyl pyruvate hydrogenation on 10,11-dihydrocinchonidine modified Pt, in toluene, increases rapidly at low $H_2$ pressures and begins to level off around 20 bar.[11]

In conclusion, we suggest that methyl pyruvate can undergo enol formation and subsequent self-assembly on Pt(111) at room temperature in the absence of a sufficient coverage of hydrogen. The initial tautomerization step, CH bond scission in the acetyl group, can be inhibited at room temperature under a sufficient $H_2$ pressure. The STM data show no evidence for an irreversible polymerization reaction. Hence, it is unlikely that rate enhancement of the enantioselective hydrogenation reaction is simply due to the absence of a substrate polymerization reaction under reaction conditions. This suggests that more study is required to seek out the origin of the rate-enhancement effect.

**Acknowledgment.** Support from NSERC, FQRNT, and CFI is gratefully acknowledged.

**Supporting Information Available:** Low temperature, hydrogen coadsorption, and high coverage STM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA072638H