Communication

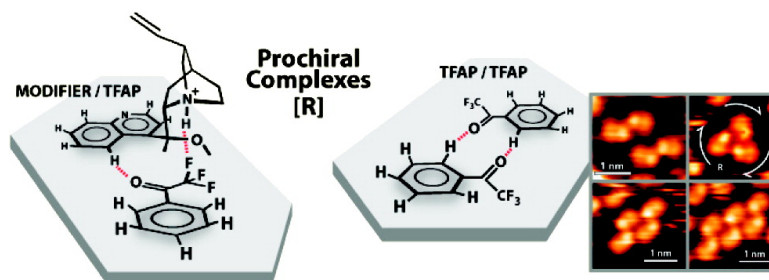# Activation in Prochiral Reaction Assemblies on Pt(111)

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Activation in Prochiral Reaction Assemblies on Pt(111)

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Striking examples of rate enhancement[1] have been reported for the enantioselective hydrogenation of activated ketones on cinchona-modified Pt catalysts, the Orito reaction.[2] In particular, most measurements show that the apparent rate of hydrogenation of ethyl pyruvate on the chirally modified metal is much greater than that for the racemic reaction on the nonmodified surface, despite the fact that the modifier partly covers the metal surface. There is, however, an ongoing debate[3] as to whether the effect is due to true rate enhancement brought about by the chiral modifier or due to a lowering of the reactivity of the nonmodified surface brought about by intersubstrate reactions.

Large differences in rate between the modified and the nonmodified surface are not a general feature of the Orito reaction.[4,5] Several groups have reported results for a class of substrates, including trifluoroacetophenone (TFAP), which display small to negligible rate enhancement.[4,5] It is noteworthy that these substrates contain a phenyl substituent α to the prochiral ketone group. In this Communication, we report scanning tunneling microscopy (STM) and density functional theory (DFT) results showing that TFAP forms room-temperature stable C−H···O bonded dimers and trimers on Pt(111). We propose that these structures mimic those formed in the cinchona−TFAP interaction, thereby accounting for the observed small rate differences.

STM images of TFAP (Figure 1A,B) show well-defined groups of two (A1,A2,B1,B2), three (A3,B1,B3,B4), four (B1,B5), or six (B6) molecules over the entire surface at room temperature. Only dimers were observed (A1) at low coverages, indicating that they are the basic unit for the larger even-numbered clusters. Left- and right-handed trimers are also observed as the coverage is increased. In B1−B6, each molecule is imaged as an elongated protrusion with a bright spot at the tapered end. In A1−A3, each molecule is imaged as a bright protrusion with a smaller dark spot at one end. The high-resolution images show that the dimers are formed from counter-aligned molecules.

The interpretation of the STM data is supported by our DFT calculations done with the DACAPO package[6a] (nonlocal exchange-correlation,[6b] a plane-wave basis, two **k**-points, ultrasoft pseudopotentials, and periodic slabs with 72 Pt atoms in three fcc(111) layers). The calculations show π-bonding of the aromatic group of TFAP to Pt(111). At coverage 1/12, that is, one TFAP per 12 surface Pt atoms, the binding energy per monomer is 1.02 eV. Forming TFAP dimers at this coverage (Scheme 1A) releases 0.22 eV per dimer. The dimer (Scheme 1A,B) binds via two C−H···O=C hydrogen bonds that are 2.38 Å long. The H···O=C angles are 148°. Calculations for trimers
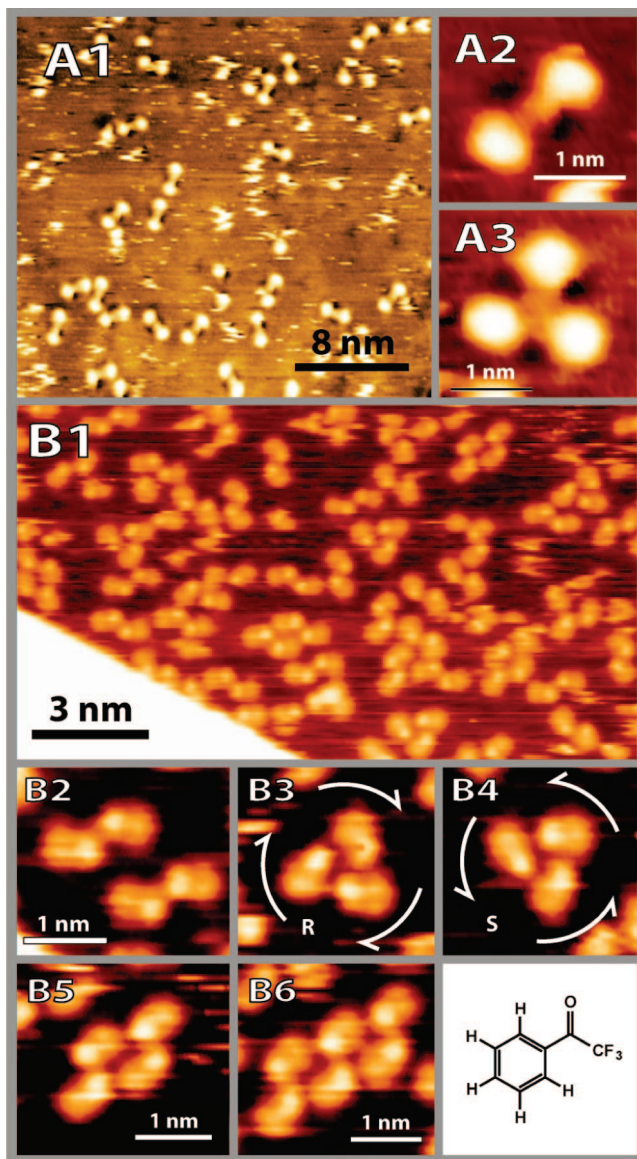

Figure 1. STM images of trifluoroacetophenone (TFAP) on Pt(111) at room temperature (bias, −1.0 V; tunnel current, 1.0 nA).

and tetramers are prohibitively large, but we envisage three C−H···O=C bonds for the trimers and C−H···F interactions between C−H···O bonded dimers for the tetramers.

The property of chemisorption activated aromatic to carbonyl C−H···O bonding was first reported, on the basis of surface spectroscopy[7a] and STM[7b] data, for carbonyl molecules coadsorbed with benzene[7a] or pyrene[7a] on Pt(111). Activation toward

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Scheme 1. (A) Calculated Trifluoroacetophenone (TFAP) Dimer Structure on a 72 Atom 3-Layer Pt(111) Slab; (B) Illustration of the Calculated Structure; (C) A Proposed Two-Point H-Bonding Model for the Stereodirecting Interactions between TFAP and Cinchonidine on Pt[10]

Prochiral Complexes [R]
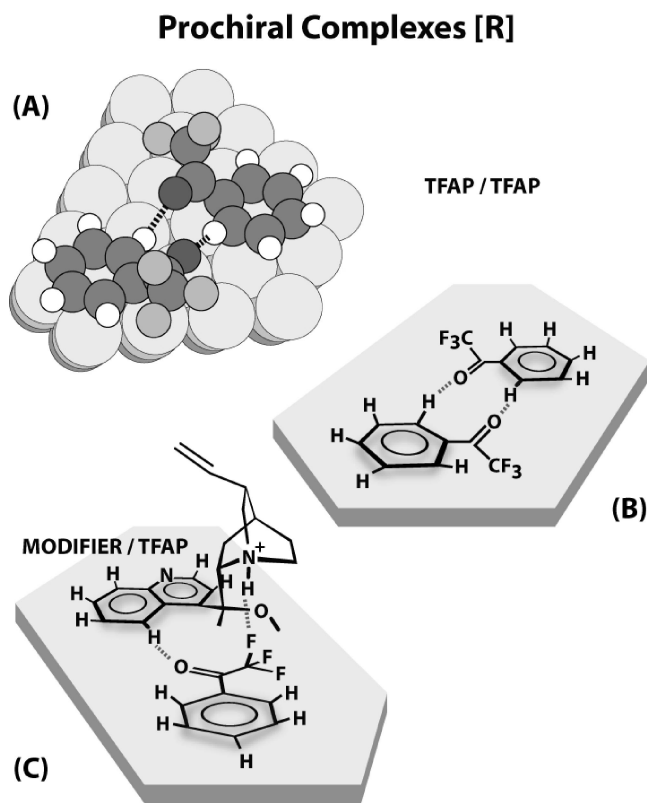
H-bonding is attributed[7] to the electron redistribution[8] brought about by the formation of the chemisorption bond.

In the case of TFAP, additional activation arises due to the electron-withdrawing nature of the substituent on the phenyl ring. Intrinsic, chemisorption-induced, C−H•••O hydrogen bonding is an expected interaction for coadsorbed aromatic and carbonyl molecules on platinum,[7] providing the aromatic chemisorbs in a π-bonded configuration. There is much evidence to support the conclusion that the chiral pocket in the Orito reaction is formed, in part, by the π-bonded aromatic anchor of the chiral modifier.[9] Hence, aromatic to carbonyl H-bonding, between the chemisorbed modifier and substrate, must be considered as a possible stereodirecting force. Along these lines, Lavoie et al.[10] proposed a two-point H-bonding model for the diastereomeric complex, as illustrated in Scheme 1C, using cinchonidine and TFAP as the chiral modifier−substrate pair.

Each TFAP dimer on the Pt(111) surface (Scheme 1A,B) is connected by a pair of donor/acceptor and acceptor/donor hydrogen bonds. The dimers are homochiral and cannot be superimposed on their mirror images without first removing them from the surface. As such, they are themselves chiral modifier−substrate pairs, present in a racemic mixture as previously reported for cysteine dimers on Au(110).[11] The combination of C−H•••O bonding and carbonyl chemisorption implicit in TFAP dimer formation mimics that for the proposed cinchonidine−prochiral carbonyl interaction (Scheme 1C), both in terms of the adsorption geometry of the carbonyl and H-bonding to the carbonyl. We propose that it is this similarity that is largely responsible for the small or negligible rate

enhancement observed for TFAP;[4] that is, the activation of the prochiral carbonyl in homomolecular TFAP assemblies at racemic sites is expected to be roughly the same as that in the diastereomeric cinchona−TFAP complex formed at chiral sites.

In contrast, while aliphatic α-ketoester substrates, such as ethyl pyruvate, cannot display intersubstrate carbonyl to aromatic H-bonding, they can form a variety of adsorbed states. For example, ethyl pyruvate might form enol,[12a] η^1(O), η^2(C,O), or π-states[12b,c] on Pt, and condensation products on supported Pt,[3] some of which may be only spectator species in the racemic hydrogenation reaction.[12b] By forming 1:1 chiral modifier−substrate complexes, nonintrinsic adsorption geometries are imposed through the compromise required to satisfy both chemisorption and supramolecular interactions. The different reaction rate at the chiral site is then partly a manifestation of the fact that adsorption geometry and chemical reactivity at surfaces are sensitively interrelated and partly a manifestation of activation of the prochiral carbonyl through H-bond[13] formation.

In summary, the observation of C−H•••O=C bonded TFAP prochiral assemblies on Pt(111) suggests a reason why α-phenyl ketone substrates do not display strong rate enhancement in the Orito reaction. This conclusion may provide some guidance in the more difficult challenge of understanding rate differences that are often observed for substrates such as ethyl pyruvate.

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