

Requirements for the Formation of a Chiral Template

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The chemisorptive enantioselectivity of propylene oxide is examined on Pd(111) surfaces templated by chiral 2-methylbutanoate and 2-aminobutanoate species. It has been found previously that chiral propylene oxide is chemisorbed enantiospecifically onto Pd(111) surfaces modified by either (*R*)- or (*S*)-2-butoxide. The enantiomeric excess (ee) varied with template coverage, reaching a maximum of ~31%. Templating the surface using 2-methylbutanoate, where the chiral center is identical to that in the 2-butoxide species, but is now anchored to the surface by a carboxylate rather than an alkoxide linkage, shows no enantiospecificity. The enantioselectivity is restored when the methyl group is replaced by an amine group, where a maximum ee value of ~27% is found. DFT calculations and infrared measurements suggest that the structures of the butyl group on the surface are similar for both 2-butoxide and 2-methylbutanoate species, implying that gross conformational changes are not responsible for differences in chemisorptive enantioselectivity. There is no clear correlation between the location of the chiral center and enantioselectivity, suggesting that differences in the template adsorption site are also not responsible for the lack of enantioselectivity. It is proposed that the 2-butyl group in 2-methylbutanoate species is less rigidly bonded to the surface than that in 2-butoxides, allowing the chiral center to rotate azimuthally. It is postulated that the role of the amino group in 2-aminobutanoate species is to anchor the chiral group to the surface to inhibit azimuthal rotation.

Introduction

The current market for enantiomerically pure compounds, primarily used for pharmaceuticals, is expected to reach almost \$9 billion by the end of 2004 and is projected to increase by more than 11% per year.¹ Catalytic processes used for their synthesis are primarily carried out in the homogeneous phase,^{2–4} and such catalysts often contain heavy metal centers, which must be removed from the product prior to use, a problem which is avoided by the use of heterogeneous catalysts. Heterogeneous catalysts must however be modified to render them enantioselective. The way in which such modifiers operate can generally be classified into two categories. In the first, the modifiers operate in a collective way to define a chiral adsorption site and are referred to in the following as templates.⁵ In the second, there is a direct enantiospecific interaction between the modifier and reactant, which is referred to as a one-to-one modifier.^{6–8} We have previously examined the properties of chiral overlayers on Pd(111) formed by the adsorption of 2-butanol.^{9,10} 2-Butanol (C₂H₅C*H(OH)CH₃, where C* is the chiral center) reacts to form a 2-butoxide species,^{11,12} and the enantioselectivity of a 2-butoxide-modified Pd(111) surface was probed in ultrahigh vacuum by adsorbing either (*R*)- or (*S*)-propylene oxide (referred to as the probe) on a surface modified by either (*R*)- or (*S*)-2-butoxide species. Preferential adsorption of one chirality of the probe (propylene oxide) onto a surface modified by 2-butoxide species of the same chirality was detected over a relatively narrow coverage range, and reached a maximum at ~30% of the saturation coverage. The enantioselectivity was measured from the ratio $R_e = \Theta_{RR}/\Theta_{RS}$, where Θ_{RR} is the saturation

coverage of (*R*)-propylene oxide on a (*R*)-2-butoxide-modified surface, and Θ_{RS} the saturation coverage of (*R*)-propylene oxide on one modified by (*S*)-2-butoxide species. The maximum value of this ratio was found to be ~1.9. This can also be written in terms of the more conventional enantiomeric excess (ee) as

$$ee = \frac{R_e - 1}{R_e + 1} \times 100$$

so that an R_e value of ~1.9 yields an ee of ~31%. The experimentally observed variation in R_e with 2-butoxy coverage was shown theoretically to be consistent with the formation of chiral templates.^{13,14} The 2-butoxide species undergoes a β -hydride elimination on heating to form a ketone, resulting in a loss of the chiral center with a concomitant loss of enantioselectivity.^{9,10}

In originally selecting 2-butanol as a chiral template, it was suggested that the minimum requirement for forming a chirally templated surface was to have an anchoring point (via an –O–Pd linkage in the case of 2-butanol) attached to a chiral center.⁹ The 2-butyl group was selected as a relatively simple example of a chiral center. This group also has the advantage mentioned above that it forms a ketone by β -hydride elimination on heating, thus allowing us to check whether the enantioselectivity disappeared with the loss of the chiral center. In the following, we examine the effects on enantioselectivity of changing the template using the same protocol, that of modifying the surface with various coverages of the chiral modifier and then measuring the adsorption of either (*R*)- or (*S*)-propylene oxide on these surfaces. 2-Methylbutanoic and 2-aminobutanoic acids are selected as chiral templates in part since they are thermally more stable than the 2-butoxide species.

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Experimental Section

The experiments were carried out in two stainless steel, ultra-high-vacuum chambers operating at base pressures of $\sim 8 \times 10^{-11}$ Torr following bakeout, which have been described in detail elsewhere.^{15,16} Reflection-absorption infrared spectroscopy (RAIRS) spectra were collected from a Pd(111) single-crystal sample mounted in a modified $2\frac{3}{4}$ in. six-way cross equipped with infrared-transparent, KBr windows. The sample could be resistively heated to 1000 K, or cooled to 80 K using liquid nitrogen. Light from a Bruker Equinox infrared spectrometer passes through a polarizer and is focused onto the sample at an incidence angle of $\sim 80^\circ$ and the reflected light steered onto the detector of a liquid nitrogen cooled, mercury-cadmium-telluride detector. The complete light path is enclosed and purged with dry, CO₂-free air. The spectrometer operated at 4 cm^{-1} resolution, and data were typically collected for 1000 scans. The infrared cell was attached to the main 12 in. diameter ultra-high-vacuum chamber, and the sample could be moved from the cell into the main chamber by means of a transfer rod. This chamber was equipped with a single-pass, cylindrical-mirror analyzer, which was used to collect Auger spectra of the sample.

Temperature-programmed desorption (TPD) data and X-ray photoelectron spectroscopy (XPS) spectra were collected in another chamber. TPD spectra were obtained using a heating rate of $\sim 7\text{ K/s}$ and desorbing species detected using a Dycor quadrupole mass spectrometer interfaced to a PC, allowing five masses to be monitored sequentially during the same desorption sweep. Molecular beam data were obtained with the same mass spectrometer and PC interface using the King and Wells method.¹⁷ XPS data were collected using a Mg anode operating at a power of 250 W and the energy of the photoelectrons analyzed using a double-pass, cylindrical-mirror analyzer operating at a pass energy of 100 eV.

The sample was cleaned using a standard procedure.¹⁵ The 2-butanol and 2-methylbutanoic acid (Acros, p.a.), racemic propylene oxide (Acros, p.a.), or pure enantiomers of propylene oxide (Aldrich, 99%) were transferred to glass vials, attached to the gas-handling line of the vacuum system, and further purified by repeated freeze-pump-thaw cycles and their purities monitored mass spectroscopically. The vapor pressure of 2-aminobutanoic acid was sufficiently low that it could not be dosed using this method and was introduced directly into the vacuum chamber from a heated vial via a heated dosing tube.

Density functional theory (DFT) calculations of the structure of 2-butoxide or 2-methylbutanoate on a cluster of atoms representing a Pd(111) surface were computed by the DMol program.¹⁸

Results

It has been shown previously that propylene oxide adsorbed onto 2-butoxy-modified Pd(111) displays a maximum R_e value of ~ 1.9 ($ee \approx 31\%$), which is exhibited over a relatively narrow coverage range.^{9,10} The role of the -OH group in the parent alcohol is to anchor the chiral 2-butyl group to the surface. Alkoxy species have been found to adsorb with the C-O bond perpendicular to the surface, generally adsorbing at a 3-fold hollow site.^{19,20} In principle, therefore, anchoring the 2-butyl group to the surface with another functionality that has the bond from the chiral carbon to the surface oriented perpendicular to the surface should yield similar enantioselectivities. The structure of formate species formed from formic acid on Pd(111) has recently been measured using low-energy electron diffraction

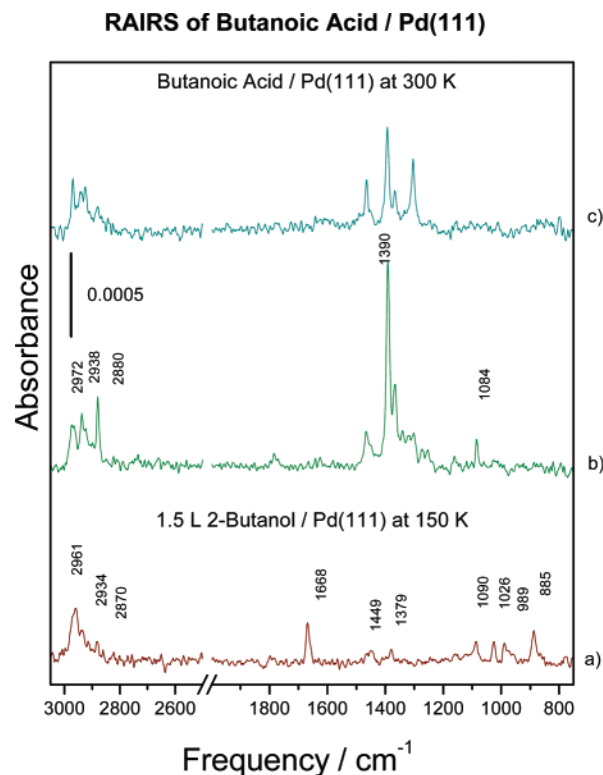


Figure 1. Reflection absorption infrared spectra of (b) 2-methylbutanoic acid (~ 0.3 monolayers relative coverage) and (c) a saturated overlayer following adsorption on Pd(111) at 300 K. Shown for comparison (a) is the RAIRS spectrum of ~ 0.3 monolayer of 2-butanol adsorbed on Pd(111) at 80 K and annealed to 150 K to form 2-butoxy species.

(LEED) and calculated by DFT, where both theory and experiment yield identical structures.²¹ It is found that the formate species bonds with the OCO plane perpendicular to the surface with the oxygen atoms located approximately above atop sites. Similar structures have been found theoretically for acetate species on palladium in which the methyl group is oriented perpendicularly to the surface.²² Templated surfaces were therefore prepared by substituting the -OH group by a carboxylic acid group (thus, by using 2-methylbutanoic acid). These are expected to form carboxylate species by removal of the proton from the acid so that the chiral carbon of the resulting 2-methylbutanoate would be located approximately above a bridge site. RAIRS spectra were collected of 2-methylbutanoic acid on Pd(111) following adsorption at 300 K (Figure 1b) and compared with previously collected spectra of 2-butoxide species on Pd(111) at a similar coverage (Figure 1a) (the coverage at which it exhibited the maximum value of R_e).⁹ These spectra will be discussed in greater detail below, but the intense 1390 cm^{-1} mode is assigned to the symmetric OCO stretching vibration of a carboxylate group and indicates that the acidic hydrogen has been removed.^{23,24} Also shown is the spectrum of a saturated overlayer of 2-methylbutanoic acid adsorbed on Pd(111) at 300 K (Figure 1c), where a similar 1390 cm^{-1} feature indicates that 2-methylbutanoate species have formed. In this case, however, differences in intensities suggest that it has undergone some structural changes at higher coverages.

Figure 2 displays the TPD spectra of a saturated overlayer of 2-methylbutanoic acid adsorbed on Pd(111) collected at various masses. The features centered at $\sim 220\text{ K}$ are due to the desorption of molecular 2-methylbutanoic acid since the relative peak intensities compare well with the mass spectrometer ionizer fragmentation pattern of the parent acid. Hydrogen

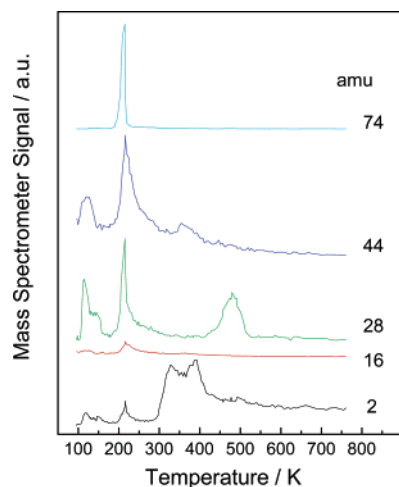


Figure 2. Temperature-programmed desorption spectra of a saturated overlayer of 2-methylbutanoic acid adsorbed on Pd(111) at 100 K collected at various masses using a heating rate of 7 K/s. The monitored masses are indicated adjacent to the corresponding spectrum.

(2 amu) and CO_2 (44 amu) desorb above 300 K, indicating that no 2-methylbutanoate decomposition is under way at 300 K. These spectra are consistent with those found for other carboxylic acids on Pd(111) surfaces,²³ and theoretical calculations indicate that decomposition takes place by hydrogen abstraction from the methyl group.²⁵

The R_e value was measured using (*R*)- and (*S*)-propylene oxide as a probe by adsorption onto (*R*)- and (*S*)-2-methylbutanoate-modified surfaces and was found to be ~ 1 ($ee = 0\%$) for all modifier coverages. That is, no enantioselectivity was measured for this modifier. As noted above, the chiral center is located above a bridge site in the case of 2-methylbutanoate species, while it is above a 3-fold hollow site in the case of 2-butoxy modifiers. In addition, the chiral butyl group is farther away from the surface when anchored by a carboxylate than an oxygen. This may allow the chiral center to rotate more freely, thereby averaging out any asymmetry that gives rise to the enantioselectivity. To examine which of these possible effects might be responsible for the loss of enantioselectivity for a 2-methylbutanoate-modified surface, the methyl group was replaced by an amine so that the surface was templated using 2-aminobutanoic acid. The absolute saturation coverage of (*R*)-2-aminobutanoic acid adsorbed at 300 K was measured from the integrated intensity of the C 1s signal compared to a saturated overlayer of CO on Pd(111),²⁶ yielding a value of 0.18 ± 0.02 monolayer (where absolute coverages are referenced to the palladium atom density on the (111) surface). 2-Aminobutanoic acid was adsorbed on the surface at 300 K to form a carboxylate where the amine bonds to the surface to completely inhibit azimuthal rotation of the chiral center. The oxygens of the carboxylate group are expected to bond to palladium atoms in a fashion similar to that of formate species. Calculations of the structure of glycine on copper surfaces show that it bonds with this geometry,²⁷ and the computed structure is in good agreement with the results of experiment.^{28–32} The measured absolute saturation coverage of 2-aminobutanoate species adsorbed at 300 K is consistent with this adsorption geometry. The enantioselectivity is probed at 150 K using the King and Wells¹⁷ method to determine the coverage of propylene oxide, and the resulting value of R_e is plotted versus absolute 2-aminobutanoate coverage in Figure 3. This now shows that the value of R_e increases from unity on the clean surface to reach a maximum value of 1.75 ± 0.08 ($ee = 27 \pm 3\%$) and then decreases once again at higher coverages. The dashed line through these data

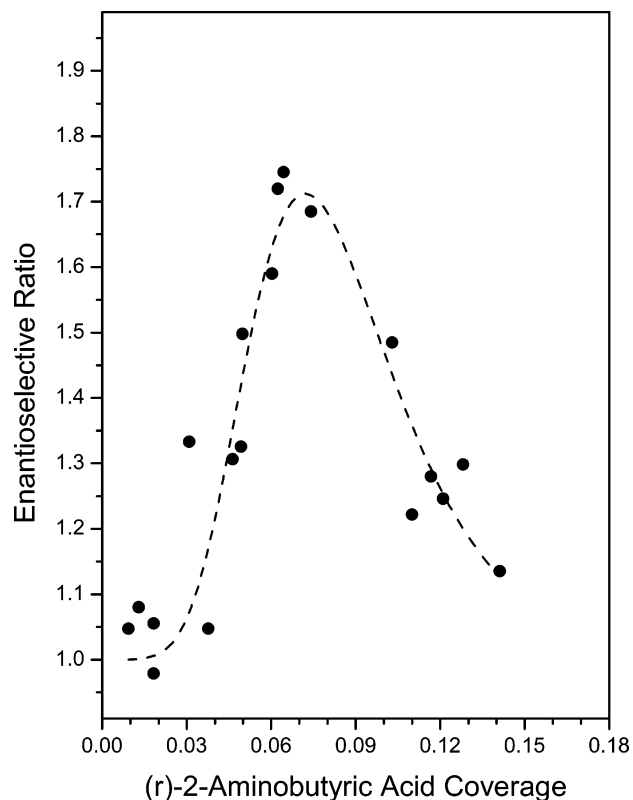


Figure 3. R_e versus coverage for the adsorption of (*R*)- and (*S*)-propylene oxide at 80 K on a surface that has been modified by 2-aminobutanoic acid to form a 2-aminobutanoate template.

TABLE 1: Assignments of the Vibrational Frequencies of 2-Butoxy and 2-Methylbutanoate Species on Pd(111)

assignment	vibrational frequency/cm ⁻¹	
	2-butoxide/ Pd(111)	2-methylbutanoate/ Pd(111)
$\nu_a(\text{CH}_3)$	2961	2972
$2\delta_s(\text{CH}_3), \nu_s(\text{CH}_3), \nu(\text{CH}_2)$	2934	2938
$\nu(\text{CH})$	2870	2880
$\delta_a(\text{CH}_3), \delta_s(\text{CH}_2)$	1449	1466
$\nu(\text{OCO})$		1390
$\delta_s(\text{CH}_3)$	1379	1365
CH_2 wag		~ 1260
CH_3 rock		1084
$\nu(\text{M}-\text{O}-\text{C})$	1090	
$\nu(\text{C}-\text{C})$	1026	
$\rho(\text{CH}_3), \rho(\text{CH}_2)$	989	
$\rho(\text{CH}_2) + \nu(\text{CO})$	885	

is included as a guide to the eye. The enantioselectivity has been restored by using an amino acid as a template where the enantioselectivity is again expressed over a relatively narrow coverage range and reaches a maximum at a relative coverage of 0.39 ± 0.07 , similar to that found for 2-butanol.^{9,10}

Discussion

A portion of the 2-methylbutanoic acid adsorbed on Pd(111) desorbs molecularly at ~ 220 K, with the remainder decomposing to desorb hydrogen and CO_2 above 300 K (Figure 2). The infrared spectrum collected following 2-methylbutanoic acid adsorption at 300 K at a relative coverage of ~ 0.3 monolayer is displayed in Figure 1b, compared with that obtained for 2-butoxide species at the same relative coverage (Figure 1a). The spectral assignments are given in Table 1.^{32,33} The intense feature at 1390 cm⁻¹ (Figure 1b) is assigned to an OCO

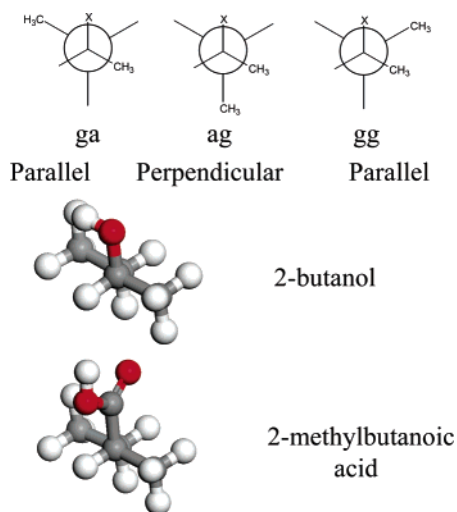


Figure 4. Depiction of the stereochemistry of $(\text{C}_2\text{H}_5)\text{C}^*\text{HX}(\text{CH}_3)$, where X is a functional group (in this case, either $-\text{O}-$ or $-\text{COO}$). The stereochemistry is depicted for the (*R*)-enantiomer, and the most stable gas-phase structures of 2-butanol and 2-methylbutanoic acid are displayed at the bottom of this figure.

vibration, indicating the formation of a surface carboxylate, and the remainder of the features are assigned to butyl vibrational modes.

Evidently there is a strong variation in the chemisorptive enantioselectivity depending on how the chiral center is anchored to the surface, with 2-butoxy templates having an R_e value of ~ 1.9 ($ee \approx 31\%$), while anchoring the chiral 2-butyl center by a carboxylate results in no enantioselectivity ($ee = 0\%$). This is restored when the methyl group is replaced by an amine to yield $R_e \approx 1.7$ ($ee \approx 27\%$), slightly lower than for 2-butanol (Figure 3). Since the carboxylate group bonds such that the chiral center is above a bridge site, while in the case of the alkoxy species it is above a 3-fold hollow site, one possible origin for this discrepancy might be the different template adsorption sites. While the structure of the 2-aminobutanoate has not been measured on Pd(111), the calculated structure of a simple amino acid (glycine) on copper²⁷ shows that the carboxylate group is similarly bonded with the oxygens bonded to palladium atoms, with the nitrogen of the amine group also coordinated to the surface. The saturation coverage of 2-amino-butanoic acid is in accord with a similar geometry on Pd(111). Tilting of the carboxylate group toward the surface to allow the nitrogen to bond to the surface would move the chiral carbon closer to an atop site so that there is no clear correlation between the location of the chiral center and the ensuing enantioselectivity. This suggests that the location of the chiral center is not likely to be the origin of the differences in enantioselectivity. Another possible origin for the effect might be differences in the structure of the chiral center. Gas-phase 2-butanol and 2-methylbutanoic acid can adopt several conformations as shown in Figure 4.³⁴ These are designated *ga*, *ag*, and *gg* ($g = \textit{gauche}$, $a = \textit{anti}$) and are illustrated for the (*R*)-enantiomer in Figure 4. Previous MP2 calculations have shown that, for 2-butanol, the *ga* conformation is ~ 0.8 kcal/mol more stable than the *ag* conformer, which in turn is ~ 1.2 kcal/mol more stable than the *gg* structure.³⁴ At 80 K (the temperature at which the experiments were carried out), the relative populations of each of the conformers of 2-butanol are (*ga*) $\sim 99\%$, (*ag*) $\sim 1\%$, and (*gg*) $\sim 0\%$. The most stable 2-butanol structure, in this case calculated by DFT, is shown in Figure 4, and is in agreement with previous results.³³ The most stable gas-phase structure of 2-methylbutanoic acid was also calculated by DFT and also

reveals that the *ga* structure was the most stable, and is also depicted in Figure 4. As noted above, the C–O bond of the butoxide and the C–COO bond of the carboxylate are both oriented normal to the Pd(111) surface. This implies that the C–CH₃ group of both 2-butoxy and 2-methylbutanoate would be oriented close to parallel to the surface in the *ga* and *gg* conformations, and close to normal to the surface in the *ag* conformation. If the most stable gas-phase conformation is maintained on the surface, this implies that the butyl groups in both cases would be oriented essentially parallel to the surface. There are some differences in relative intensities of the vibrational features due to the 2-butyl group for 2-butoxide (Figure 1a) and 2-methylbutanoate (Figure 1b). The initial formation of a ketone from decomposition of the 2-butoxy species (Figure 1a) is evidenced by the appearance of a feature at 1668 cm^{-1} (Figure 1a). The major differences between the two spectra are the features at 885 , 989 , and 1026 cm^{-1} for 2-butoxide, not detected for 2-methylbutanoate. The 885 cm^{-1} feature is assigned to a combination of the CH₂ rocking and CO stretching modes, and its intensity is therefore enhanced due to the presence of the C–O–Pd linkage in the butoxide. The carbon–carbon stretching vibration, visible at 1026 cm^{-1} in the 2-butoxide species (Figure 1a), is not detected for the carboxylate (Figure 1b), but this mode may couple with the C–O vibration, thereby enhancing its intensity. Similarly, CH₃ and CH₂ rocking modes are detected at $\sim 989\text{ cm}^{-1}$ for 2-butoxide, not seen for the carboxylate. Again, this may be due to coupling with the C–O stretching mode. The 2938 cm^{-1} mode is more intense for 2-methylbutanoate than for the 2-butoxide, but this is due to several modes so that it is difficult to assign these differences to different molecular orientations. The clearest difference in the C–H stretching region is the intense mode at 2880 cm^{-1} for 2-methylbutanoate, which is very weak for the 2-butoxide species. However, the difference between the various conformers involves rotation around the C–C bond joining the chiral carbon and the ethyl group (Figure 4), so it should not result in differences in the orientation of the C–H bond with respect to the surface. This could be indicative of a tilting of the OCO plane toward the surface, although a substantial tilt would be required to yield such a large intensity difference, resulting in a substantial steric interference between the methyl and ethyl groups and the surface. Therefore, to gain further insight into the relative geometries of 2-butoxide and 2-methylbutanoate species, DFT calculations were carried out for these species adsorbed on palladium clusters. These calculations were initially carried out for a slab of 14 palladium atoms where the Pd–Pd distance was fixed at the bulk palladium value (2.75 \AA) to carry out an initial structure determination. Subsequent calculations were carried out for 22 palladium atoms to include a second layer. Again, the Pd–Pd distance was fixed at 2.75 \AA . In the case of 2-butoxide species adsorbed on the Pd₁₄ cluster, the *ga* structure was found to be the most stable, as was found for gas-phase 2-butanol. The *gg* and *ag* structures were found to have an energy of ~ 2 kcal/mol greater than the *ga* structure, with the *ag* structure being slightly less stable than the *gg* conformer. Including a second layer of palladium atoms to form a Pd₂₂ cluster did not change the *order* of the energies of the different conformers, but did change the energy difference somewhat so that the *gg* structure is ~ 1 kcal/mol less stable than *ga*, and the *ag* conformer is now ~ 3 kcal/mol less stable than *ga*, giving a Boltzmann population of 100% for the *ga* conformation at 80 K. Activation barriers were calculated for conversion between the conformers, yielding $E_{\text{act}}(\textit{ga}-\textit{ag}) \approx 8\text{ kcal/mol}$ and E_{act}

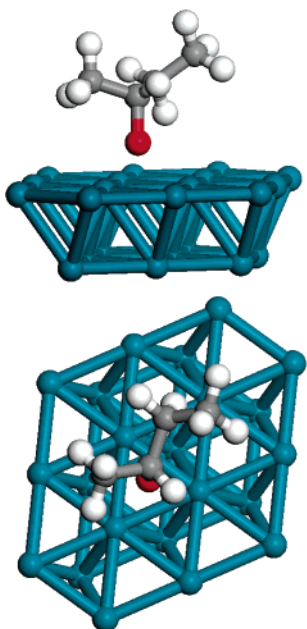


Figure 5. Depictions of the most stable structures of 2-butoxide groups on Pd(111) calculated using density functional theory.

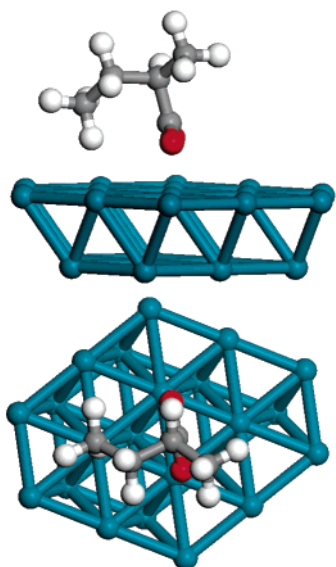


Figure 6. Depictions of the most stable structures of 2-methylbutanoate on Pd(111) calculated using density functional theory.

(*gg-ag*) \approx 6 kcal/mol. These values are rather high and suggest that an unstable conformer could be trapped in a metastable configuration, but since the most stable gas-phase and surface conformers are identical, this is unlikely. Finally, it was found that the face-centered-cubic (fcc), 3-fold hollow site was the most stable in all cases, and the final structure is displayed in Figure 5.

Similar DFT calculations were carried out for 2-methylbutanoate, initially on a Pd₁₄ cluster where the ordering of the energies of the conformers was identical to that of the 2-butoxide species, with the *ga* conformer being more stable by \sim 2 kcal/mol than the *gg* conformer, and \sim 5 kcal/mol more stable than the *ag* structure, again suggesting that the Boltzmann population of the *ga* conformer will be 100% at 80 K. Carrying out the calculation with a 22-atom cluster only slightly changes the energies, and the most stable structure is depicted in Figure 6. The structures of both species are very similar, although the ethyl group tilts somewhat more toward the surface in 2-

methylbutanoate than in the 2-butoxide. Nevertheless, the footprints of both 2-butoxide and 2-methylbutanoic templates, as gauged from the top view, are essentially identical, suggesting that conformational differences are not responsible for the differences in chemisorptive enantioselectivity of the two species.

An alternative explanation for the observation that 2-aminobutanoic acid forms an enantioselective template, while 2-methylbutanoic acid does not, is that azimuthal rigidity with respect to the surface is important in expressing enantioselectivity since free azimuthal rotation with respect to the surface will average out any asymmetry. In this case, the role of the amine group in 2-aminobutanoate is to anchor the chiral center to the surface to prevent it from rotating. Since the 2-butyl group in 2-butoxide species is closer to the surface than in the 2-methylbutanoate, the activation energy for azimuthal rotation may be higher in the former case than the latter so that, in this case, van der Waals interactions perform the same role as the amino group in inhibiting azimuthal rotation of the chiral center. The azimuthal rotational energies of the 2-butyl groups of the 2-butoxide and 2-methylbutanoate species were not calculated using DFT methods since much of this interaction will be due to van der Waals forces, which are not modeled particularly well by DFT. This postulate implies that the minimum requirement for an effective chiral template is that it bond to the surface sufficiently rigidly to prevent azimuthal rotation of the chiral center. In the case of 2-butoxy species, this is achieved by van der Waals interactions between the 2-butyl group and the surface, while in the 2-aminobutanoate species, bonding of the amine group prevents rotation.

Conclusions

While 2-butoxide species on Pd(111) provide an enantioselective template for the adsorption of propylene oxide, 2-methylbutanoate species adsorbed onto the surface do not. The enantioselectivity is restored when the methyl group is replaced by an amine group where a maximum R_e value of \sim 1.7 is found. DFT calculations suggest that the structures of the 2-butyl group on the surface are similar for both 2-butoxide and 2-methylbutanoate species, implying that gross conformational changes are not responsible for differences in chemisorptive enantioselectivity. Since there is no clear correlation between the location of the chiral center and the resulting chemisorptive enantioselectivity, this implies that differences in the template adsorption site are also not responsible for the loss of enantioselectivity for 2-methylbutanoate species. The most likely explanation for this effect, therefore, is that the 2-butyl group in 2-methylbutanoate species is less rigidly bonded to the surface than that in 2-butoxides, allowing it to rotate more freely, so that the role of the amino group in 2-aminobutanoate species is to anchor the chiral group to the surface to inhibit azimuthal rotation.

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