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Structure-sensitive enantiospecific adsorption on naturally chiral Cu(*hkl*)^{R&S} surfaces

Andrew J Gellman^{1,2}, Ye Huang¹, Anjanette J Koritnik¹ and Joshua D Horvath¹

¹ Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

² W.E. Scott Institute for Energy Innovation, Carnegie Mellon University, Pittsburgh, PA 15213, USA

E-mail: gellman@cmu.edu

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Abstract

The desorption kinetics of a chiral compound, *R*-3-methylcyclohexanone (*R*-3MCHO), have been measured on both enantiomers of seven chiral Cu(*hkl*)^{*R&S*} surfaces and on nine achiral Cu single crystal surfaces with surface structures that collectively span the various regions of the stereographic triangle. The naturally chiral surfaces have terrace-step-kink structures formed by all six possible combinations of the three low Miller index microfacets. The chirality of the kink sites is defined by the rotational orientation of the (1 1 1), (1 0 0) and (1 1 0) microfacets forming the kink. *R*-3MCHO adsorbs reversibly on these Cu surfaces and temperature programmed desorption has been used to measure its desorption energetics from the chiral kink sites. The desorption energies from the *R*- and *S*-kink sites are enantiospecific, $\Delta\Delta E_{des}^{S-R} = \Delta E_{des}^S - \Delta E_{des}^R \neq 0$, on the chiral surfaces. The magnitude of the enantiospecificity is $\left|\Delta\Delta E_{des}^{S-R}\right| \approx 1$ kJ mol⁻¹ on all seven chiral surfaces. However, the values of $\Delta\Delta E_{des}^{S-R}$ are sensitive to elements of the surface structure other than just their sense of chirality as defined by the rotational orientation of the low Miller index microfacets forming the kinks; $\Delta\Delta E_{des}^{S-R}$ changes sign within the set of surfaces of a given chirality.

Keywords: chiral, enantiospecific, surface, adsorption energy, disymmetry

(Some figures may appear in colour only in the online journal)

1. Introduction

The sensitivity of surface chemistry to surface structure is one of the most interesting problems in surface science and the unequivocal demonstration of structure sensitivity is perhaps one of the most important early achievements in the field. For example, it has been well documented that the presence of steps on single crystalline surfaces can result in surface chemistry that is much different from that observed on the flat, low Miller index metal surfaces [1, 2]. Surface structure influences adsorbate orientation, adsorption and desorption energetics, surface reaction energetics, reaction barriers and reaction selectivity. Understanding of these effects is a key motivator of many fundamental studies of surface chemistry, heterogeneous catalysis and electrochemistry. The influence of surface structure manifests itself through both the symmetry of surfaces and the distribution of different types of adsorption sites such as kinks, steps and terraces on surfaces. Herein, we explore the role of adsorption site *dissymmetry*, the property of structures lacking mirror symmetry and, therefore, having non-superimposable mirror images. Such adsorption sites are chiral resulting in enantiospecific adsorption of chiral molecules [3–7].

Enantiospecific adsorption energies, surface reaction energies and activation barriers are the origin of enantioselectivity in the chemistry of chiral and prochiral molecules on chiral surfaces. Interest in enantioselective surface chemistry stems from the fact that all of the complex biomolecules which form



Figure 1. The stereographic projection enumerating all facecentered cubic surfaces and showing the locations of the 16 surface orientations studied in this work. The inset to the upper left shows the structure of *R*-3-methylcyclohexanone (*R*-3MCHO) used to probe surface structure and chirality. Flat surfaces are denoted by open squares, stepped surfaces by open diamonds, and kinked surface by circles. The kinked surfaces with *S*-chirality are denoted by solid circles. Their *R*-enantiomorphs lie in the stereographic triangles created by reflection through any one of the edges. The dotted lines divide the stereographic triangle into six regions within which the ideal surface structures all have the same structural motif defined by which of the (111), (100) and (110) planes form the terrace, step and kink microfacets.

the building blocks of life on Earth (proteins, sugars, DNA, amino acids, etc) are homochiral; in nature they only exist in one enantiomeric form. Because chiral biomolecules interact enantiospecifically with other chiral compounds, it is necessary to produce bioactive compounds such as pharmaceuticals and agrochemicals in enantiomerically pure form [8, 9]. This requires enantioselective chemical processes such as enantioselective catalysis, separation and purification, many of which rely on chiral surfaces. The development of new chiral surfaces for enantioselective chemical processing requires an understanding of the role of surface structure in controlling enantiospecific adsorption and reaction energetics. The body of work represented herein is the most comprehensive study to date of structure sensitive, enantiospecific adsorption of a chiral molecule on naturally chiral surfaces of varying structure.

Surfaces can have naturally chiral structures, provided that they have no mirror symmetry planes orthogonal to the surface. Lacking such mirror symmetry planes, the two mirror images of the surface are nonsuperimposable and thus, chiral. Metals have highly symmetric crystal structures with multiple mirror symmetry planes and, as a result, they are *achiral* in the bulk. Nonetheless, it is possible to create naturally chiral, single crystal metal surfaces with no perpendicular mirror symmetry planes [3–7, 10, 11]. Figure 1 illustrates the stereographic triangle used to enumerate all possible surfaces that can be cleaved from a crystal; in this case, one having a face-centered-cubic (FCC) bulk structure. Every point in or on the stereographic triangle uniquely represents one of the infinite number of possible surface orientations. The points on the vertices are the high symmetry, low Miller index surfaces whose ideal surface structures have multiple perpendicular mirror planes. The surfaces represented by points on the perimeter of the triangle have one perpendicular mirror plane. The surfaces represented by the points in the interior of the triangle have ideal structures that lack mirror symmetry and, therefore, are chiral. The counterclockwise rotational relationship between the $(111) \rightarrow (100) \rightarrow (110)$ planes at the vertices of this triangle defines the *S*-chirality of the surfaces represented by points in its interior. Note that the full representation of all possible surface structures that can be cleaved from an FCC lattice requires both the triangle illustrated in figure 1 and its mirror image through any of its three edges. The surfaces represented by points in the interior of that mirror image triangle all have *R*-chirality.

Naturally chiral metal surfaces have structures based on terraces, steps and kinks formed by microfacets of the three, high symmetry, low Miller index planes: (111), (100) and (110). The interior of the stereographic triangle is broken into six zones, separated by the dotted lines in figure 1. The ideal surface structures in these zones are differentiated by the permutations of the three low Miller index microfacets forming the terrace, step or kink. Within each zone, the surfaces are differentiated by the width of the terraces separating the steps and by the length of the straight step edges separating the kinks. The $(531)^{S}$ surface at the middle of the triangle is chiral but is formed by three low Miller index microfacets that are only one unit cell wide and, therefore, cannot be classified meaningfully as terrace, step or kink features. Because the high Miller index surfaces in the interior of the stereographic triangle are chiral, they exist in two enantiomeric forms $M(hkl)^R$ and $M(hkl)^{S}$ which can interact enantiospecifically with a given enantiomer of a chiral adsorbate. In order to probe the influence of surface structure on enantiospecific adsorption, we have studied the adsorption and desorption of a chiral probe molecule, R-3-methylcyclohexanone (R-3MCHO, figure 1, upper left), on a set of 23 Cu(hkl) surfaces including both enantiomers of the seven chiral surfaces indicated with solid symbols in the stereographic triangle of figure 1 and on the nine achiral surfaces indicated with open symbols on its perimeter. Herein, we present new results of measurements of R-3MCHO desorption kinetics from Cu(100) and its vicinal surfaces: Cu(511), Cu(410), Cu(821)^{R&S} and Cu(17,5,1)^{R&S}. In addition, we use this opportunity to make a comprehensive comparison of these data with previously published data collected from the $Cu(531)^{R\&S}$ surfaces and from the surfaces vicinal to the Cu(110) and Cu(111) poles [12–14].

Since the first demonstration of the chirality of high Miller index metal surfaces [3], there have been a number of demonstrations of enantiospecific and enantioselective surface chemistry on naturally chiral metal surfaces. *R*-3MCHO is certainly the most carefully studied chiral molecular probe of enantioselectivity on chiral metal surfaces [12–17]. *R*-3MCHO adsorbs molecularly on Cu surfaces and desorbs during heating with kinetics that are sensitive to surface structure. One of the attractive features of *R*-3MCHO as a probe of adsorption sites on Cu surfaces is that temperature programmed desorption (TPD) spectra reveal up to three peaks that can be definitively assigned to desorption from flat terraces, straight close-packed step edges or kinks. If the kinks are chiral, the desorption kinetics are enantiospecific and one is able to estimate the enantiospecific desorption energies, $\Delta\Delta E_{des}^{S-R} = \Delta E_{des}^S - \Delta E_{des}^R$ from chiral surfaces distributed across the six zones of the stereographic projection (figure 1) [12–14]. In addition to exploring variations of the enantiospecific $\Delta\Delta E_{des}^{S-R}$ across the stereographic triangle, the results compiled in this work test the hypothesis that the enantiospecific preference for adsorption on these surfaces is dominated by the configuration of the microfacets and thus, the chirality of the kinks. In other words, it tests the hypothesis that, while the magnitude of $\Delta\Delta E_{des}^{S-R}$ might vary across the interior of the stereographic projection, its sign does not.

2. Experimental

Measurements of the desorption kinetics and energetics of R-3MCHO were made on a set of Cu single crystal surfaces that includes the three low Miller index planes indicated by the vertices of the stereographic triangle (figure 1), six achiral high Miller index surfaces represented by the points on the perimeter of the triangle, and both enantiomorphs of the seven chiral surfaces denoted by the points in the interior of the triangle. In total, this represents a set of 23 Cu single crystal surfaces. These single crystals are all disks of ~1 cm diameter and ~2 mm thickness. Note that for the chiral single crystals, if one side of the disk has the orientation $(hkl)^R$, then the opposite side is $(hkl)^{S}$. Thus, accurate measurements of enantio-specific $\Delta\Delta E_{des}^{S-R}$ can be made by comparing measurements of R-3MCHO desorption kinetics from the two sides of one single crystal. The ideal control measurement to demonstrate that enantiospecific differences observed between the two sides of the crystal arise purely from chirality would be to perform equivalent experiments using S-3MCHO and to observe diastereomerism, i.e. the kinetics for $R/R \equiv S/S \neq R/S \equiv S/R$, where the notation denotes 'molecular enantiomer/surface enantiomer.' Unfortunately, S-3MCHO is not available and so prior work has relied on control experiments using racemic *RS*-3MCHO to demonstrate that $RS/R \equiv RS/S$ [12, 16]. True diastereomerism in these types of experiments has been demonstrated using both enantiomers of chiral probe molecules such as propylene oxide [16], tartaric acid [18, 19], and amino acids [20, 21] on such chiral surfaces.

All Cu(*hkl*) surfaces were prepared in ultra-high vacuum using Ar⁺ sputtering and annealing treatments to generate clean, single crystalline surfaces [12–15]. Surface cleanliness was determined using x-ray photoemission spectroscopy. The orientations of the chiral surfaces were determined using low energy electron diffraction and bulk x-ray diffraction methods [22]. *R*-3MCHO vapor was introduced into the UHV chambers using leak valves and the crystal surfaces were held at temperatures >160K to avoid the adsorption of *R*-3MCHO multilayers. Once the surface was saturated with one monolayer of adsorbed *R*-3MCHO, TPD spectra were obtained by positioning the Cu surfaces in front of the aperture to a quadrupole mass spectrometer and then heating the surfaces at 1 K s^{-1} while using the signal at m/q = 39 to monitor the rate of *R*-3MCHO desorption as a function of temperature [12–14].

3. Results

We present a comprehensive set of R-3MCHO TPD spectra obtained at monolayer coverage from 23 different Cu(hkl) surfaces systematically chosen to span the variety of surface structures represented by the stereographic triangle (figure 1). The organization of the presentation begins with surfaces vicinal to Cu(111) [12], followed by surfaces vicinal to Cu(110) [14], those vicinal to Cu(100) and finally, presentation of the data from $Cu(531)^{R\&S}$ [13]. The initial context for discussing these results will be the classification of surface structures as *flat, stepped* or *kinked* based on the convention proposed by Jenkins et al [10]. In their convention, flat surfaces are those whose ideal structures contain close-packed rows of atoms running in two or more directions. Stepped surfaces are those containing close-packed rows running in only one direction. Finally, kinked surfaces are those that do not have any closepacked directions. The second context for discussing these results will be the enantioselectivity of the dissymmetric and, therefore, chiral kinked surfaces.

3.1. R-3MCHO desorption from surfaces vicinal to Cu(111)

R-3MCHO desorption kinetics from clean Cu surfaces vicinal to Cu(111) were determined from TPD spectra such as those illustrated in figure 2 [12]. R-3MCHO was adsorbed on the clean Cu surfaces at temperatures (>160K) that precluded the formation of adsorbed multilayers. Prior work has shown that R-3MCHO adsorbs molecularly on the Cu surfaces and desorbs reversible at temperatures in the range 230-400K without undergoing any decomposition [12-17]. The flat, hexagonally close-packed Cu(111) surface exhibits R-3MCHO desorption in a single peak at $T_p = 230$ K. The peak temperature is independent of coverage indicating simple first-order desorption kinetics. A low intensity, high temperature feature extending to ~350K is attributed to desorption from residual step edges on the Cu(111) surface. The TPD spectra from Cu(221) and Cu(533) are almost identical to one another, exhibiting a dominant desorption peak at $T_p = 345$ K and a broad lower temperature feature centered at ~250K. The similarity is not surprising given that the structures of the Cu(221) and Cu(533) surfaces are very similar, consisting of (111) terraces separated by close-packed, monatomic (110) and (100) step edges, respectively. These data suggest that the interaction of R-3MCHO with straight close-packed step edges results in a higher adsorption energy than on the (111) terraces and, therefore, a higher desorption temperature than from the (111) terraces. The low temperature features at ~250K observed in the TPD spectra from Cu(221) and Cu(533) are attributed to molecules desorbing from terraces that are wide enough to accommodate one or more



Figure 2. *R*-3MCHO TPD spectra from Cu(*hkl*) surfaces vicinal to the Cu(111) plane. The ideal structures of these surfaces are shown to the right. The flat Cu(111) surface reveals a single TPD peak at ~230 K. The stepped Cu(221) and Cu(533) surfaces reveal dominant peaks at ~345 K associated with desorption from close-packed step edges. The kinked surfaces reveal desorption features at 345 K associated with desorption from close-packed step edges and features at ~385 K associated with desorption from kinks sites. Heating rate was 1 K s⁻¹ and the *R*-3MCHO desorption rate was monitored using m/z = 39. Reprinted with permission from [12]. Copyright 2004 American Chemical Society.

rows of *R*-3MCHO, in addition to that bound to the step edge. The Cu(653)^{*R*&S} and Cu(643)^{*R*&S} surfaces, having no close-packed directions, are kinked. Furthermore, they lack mirror symmetry are, therefore, chiral. The TPD spectra from Cu(653)^{*R*} and Cu(643)^{*R*} surfaces exhibit *R*-3MCHO desorption features at ~250K attributable to desorption from flat (111) terraces; features at $T_p = 345$ K attributable to desorption from the close-packed step edges; and a new feature at $T_p = 385$ K that is attributed to desorption of molecules bound to the kink sites. In addition to the clear implications of the TPD spectra, adsorption energetics calculated using DFT are consistent with this assignment [23].

The TPD spectra from $\text{Cu}(653)^R$ and $\text{Cu}(643)^R$ surface reveal some features that are surprising, given their apparently similar structures. $\text{Cu}(653)^R$ has (110) step edges with (100) kinks, while $\text{Cu}(643)^R$ has (100) step edges with (110) kinks. The *R*-chirality is dictated by the clockwise sense of rotation of the $(111) \rightarrow (100) \rightarrow (110)$ microfacets. The ideal structures of the $\text{Cu}(653)^R$ and $\text{Cu}(643)^R$ surfaces have comparable areal densities of kinks. However, the apparent density of kinks on the $\text{Cu}(653)^R$ surface, as indicated by the intensity of the desorption peak at $T_p = 385$ K, is significantly lower than on the $\text{Cu}(643)^R$ surface. Presumably, this is a result of thermal roughing of the ideal structures and a greater reduction in the density of kinks on $\text{Cu}(653)^R$ than on $\text{Cu}(643)^R$ [24].

3.2. R-3MCHO desorption from surfaces vicinal to Cu(110)

The ideal structures of the surfaces vicinal to Cu(110) and the R-3MCHO TPD spectra from these surfaces are illustrated in figure 3. The Cu(110) surface has a row and trough structure with close-packed rows running in only one direction. Although it is a low Miller index surface, in the convention of Jenkins et al it has a stepped structure because the rows run in only one direction [10]. Interestingly, the desorption of R-3MCHO from the Cu(110) surface (figure 3) is dominated by a peak at $T_p = 340 \text{ K}$ [14], very similar to its desorption temperatures from the stepped Cu(533) and Cu(221)surfaces vicinal to the Cu(111) plane (figure 2). The addition of close-packed step (111) edges on the Cu(771) does not change the R-3MCHO TPD spectrum significantly from that obtained from the Cu(110) surface. The interaction of *R*-3MCHO with both Cu(110) and Cu(771) is as though they are both stepped surfaces.

The presence of (100) step edges separating (110) terraces on the Cu(430) surface eliminates any close-packed directions from the surface structure. In the Jenkins *et al* convention the Cu(430) surface is considered to be kinked. However, because there is a mirror plane oriented perpendicular to the (100) steps, the Cu(430) surface is not chiral. The desorption of *R*-3MCHO from the Cu(430) surface exhibits peaks at both $T_p = 340$ K and 380 K consistent with desorption from



Figure 3. *R*-3MCHO TPD spectra from Cu(*hkl*) surfaces vicinal to the Cu(110) plane. The ideal structures of these surfaces are shown to the right. The Cu(110) and Cu(771) surfaces each reveal a single TPD peak at ~340 K associated with desorption from stepped surfaces. The Cu(430), Cu(651)^{*R*} and Cu(17,5,1)^{*R*} surfaces reveal peaks at ~345 K associated with desorption from close-packed step edges and peaks at higher temperatures associated with desorption from kinks. Heating rate was 1 K s⁻¹ and the *R*-3MCHO desorption rate was monitored using m/z = 39. Reprinted with permission from [14]. Copyright 2011 Springer.

stepped (110) terraces and (100) step edges that are not close-packed and, therefore, kinked. Finally, the Cu(651)^{R&S} and $Cu(13,9,1)^{R\&S}$ surfaces are kinked and chiral. They also exhibit two high temperature desorption peaks attributable to desorption from stepped (110) terraces and kinks. Some of the variability of the desorption temperatures associated with molecules adsorbed on the (110) terraces is probably associated with the fact that these experiments are done on different single crystals, with different thermocouples. The variability of the desorption temperatures associated with R-3MCHO desorbing from kinks also arises from the fact that the kinks all have different structures. As will be shown, the standard error of the mean of temperature estimates made on any single surface is $\sigma_{\rm T}^{\rm sem} < 0.25 \, {\rm K}$, much less that the range of temperatures observed for R-3MCHO desorption from close-packed step edges or kinks of differing structure.

3.3. R-3MCHO desorption from surfaces vicinal to Cu(100)

The ideal structures of the surfaces vicinal to Cu(100) and the *R*-3MCHO TPD spectra from these surfaces are shown in figure 4. The Cu(100) has close-packed rows running in two directions and is flat in the convention of Jenkins *et al* [10]. Consistent with this view, *R*-3MCHO desorbs from Cu(100) with a single dominant desorption feature at $T_p = 240$ K. The addition of close-packed (111) step edges separating the (100) terraces on the Cu(511) surface results in an *R*-3MCHO TPD spectrum that is dominated by a single desorption peak at $T_p = 345$ K associated with *R*-3MCHO desorbing from close-packed step edges.

The Cu(410) surface is kinked because it has no closepacked directions, however, it is not chiral because it has a mirror plane running perpendicular the (110) step edges. The *R*-3MCHO TPD spectrum from the Cu(410) surface has the expected high temperature feature associated with desorption from kinks at $T_p = 405$ K. It also has a feature at $T_p = 345$ K which we attribute to desorption from close-packed (111) step edges generated by roughening of the (110) steps [24–26]. Finally, the desorption spectra from the Cu(821)^{*R*} and Cu(17,5,1)^{*R*} surfaces both show features associated with desorption from close-packed steps and from kinks. Note that the Cu(17,5,1)^{*R*} surface has non-close-packed (110) steps and *R*-3MCHO desorption at $T_p = 405$ K, just like the Cu(410) surface. The desorption features at T < 300 K on these kinked surfaces are broad and complex.

3.4. Enantiospecific R-3MCHO desorption from chiral kinked surfaces

The enantiospecific desorption of *R*-3MCHO has been measured from the *R*- and *S*- enantiomers of the six chiral surfaces shown in figures 2–4 and from the Cu(5 3 1)^{*R*&S} surfaces. Because the opposing faces of these single crystals are of opposite chirality, differences in the peak desorption temperatures can be measured with a high degree of accuracy. For each crystal, *R*-3MCHO desorption was measured 5 or 6 times



Figure 4. R-3MCHO TPD spectra from Cu(hkl) surfaces vicinal to the Cu(100) plane. The ideal structures of these surfaces are shown to the right. The Cu(100) surface reveals a single TPD peak at ~240K associated with desorption from a flat surface. Cu(511) reveals a desorption peak at ~345 K associated with desorption from close-packed step edges. The Cu(410), Cu(821)^R and Cu(17,5,1)^R surfaces reveal peaks at ~345 K associated with desorption from close-packed step edges and peaks at higher temperatures associated with desorption from kinks. Heating rate was 1 K s⁻¹ and the *R*-3MCHO desorption rate was monitored using m/z = 39.

	$T_{\rm p}^S$	σ_T^S	$T_{\rm p}^R$	σ_T^R	ΔT_p^{S-R}	$\Delta E_{\rm des}^S$	$\Delta E_{\rm des}^R$	$\Delta \Delta E_{\rm des}^{S-R}$
Surface	Kink site (K)					Kink site (kJ mol ⁻¹)		
Cu(643)	386.4 ^a	0.7 ^b	383.1	0.4	$3.3\pm0.7^{\circ}$	104.1 ^d	103.2	$0.89\pm0.18^{\mathrm{e}}$
Cu(653)	386.3	0.5	383.2	0.3	3.1 ± 0.5	104.1	103.2	0.85 ± 0.14
Cu(651)	367.5	0.6	365.1	0.4	2.3 ± 0.6	98.9	98.2	0.64 ± 0.16
Cu(13,9,1)	384.0	0.6	386.4	0.5	-2.3 ± 0.7	103.5	104.1	-0.65 ± 0.20
Cu(17,5,1)	404.5	0.8	402.1	1.0	2.3 ± 1.0	109.1	108.5	0.65 ± 0.28
Cu(821)	381.8	1.6	385.7	1.9	-3.9 ± 1.3	102.9	103.9	-1.08 ± 0.36
Cu(531)	372.7	0.4	370.5	0.4	2.3 ± 0.4	100.3	99.7	0.63 ± 0.12
	Step site (K)					Step site (kJ mole $^{-1}$)		
Cu(643)	349.1	1.0	347.9	0.8	1.2 ± 1.0	93.8	93.4	0.33 ± 0.28
Cu(653) ^f								
Cu(651)	343.9	0.2	343.5	0.6	0.4 ± 0.7	92.2	92.4	0.12 ± 0.20
Cu(13,9,1)	347.4	0.6	347.9	0.8	-0.5 ± 0.9	93.4	93.3	-0.13 ± 0.24
Cu(17,5,1)	344.9	0.7	344.8	1.1	0.1 ± 1.1	92.6	92.6	0.02 ± 0.26
Cu(821)	345.7	0.9	344.5	1.3	1.2 ± 0.9	92.5	92.8	0.33 ± 0.24
Cu(531)	343.8	0.5	344.6	0.7	-0.8 ± 0.6	92.5	92.3	-0.23 ± 0.18

Table 1. Peak desorption temperatures (K) and desorption energies $(kJ mol^{-1})$ for R-3MCHO desorption from the step site and the kink sites on the two enantiomorphs of seven chiral $Cu(hkl)^{R\&S}$ surfaces.

 ${}^{a}T_{p}$ are averages of 5–6 measurements on each surface.

 ${}^{b}\sigma_{T}$ are standard deviations of the set of measurements of T_{p} .

^cRanges on ΔT_p^{S-R} are 95% confidence intervals estimated from $2\sqrt{(\sigma_T^R)^2/N^R + (\sigma_T^S)^2/N^S}$. ^dValues of ΔE_{des} were estimated from T_p using the Redhead equation and a value of 10^{13} s⁻¹ for the desorption pre-exponential factor [30].

^eRanges on $\Delta\Delta E_{des}$ are 95% confidence intervals.

^fBecause the *R*-3MCHO desorption temperatures from the kink and step sites on Cu(653)^{*R&S*} are so close, it was necessary to measure the desorption kinetics from the kinks under low coverage conditions at which the steps were not fully saturated with R-3MCHO. Thus, insufficient data is available for *R*-3MCHO desorption from the $Cu(653)^{R\&S}$ step sites.

on each side in order to determine the standard deviation of the peak temperatures, T_p , measured for desorption from the chiral kinks [12–14, 16]. The standard deviation of the measured values of T_p from a given surface was typically $\sigma_T = 0.6$ K. For N = 6 measurements of a given T_p , the standard error of the mean is $\sigma_T^{\text{sem}} = \sigma_T / \sqrt{N} = 0.25$ K yielding a 95% confidence interval of $\pm 2\sigma_T^{\text{sem}} = 0.5$ K for the value of T_p estimated by the mean of the individual measurements. Mean values of T_p^R and T_p^S from the *R*- and *S*-enantiomorphs of a chiral surface, $\left|T_p^S - T_p^R\right|$, that differ by more than $2\sqrt{2}\sigma_T^{\text{sem}} = 0.7$ K indicate enantiospecific desorption with >95% confidence. Values for the mean are listed for each surface in table 1.

As an example of enantiospecific desorption from a surface vicinal to Cu(110), figure 5 shows the *R*-3MCHO TPD spectra from the Cu(13,9,1)^{*R*&S} surfaces. The temperatures of the desorption peak maxima have been found by fitting Gaussian curves to the peaks and averaging over six independent measurements. The desorption peak temperatures from the chiral kinks are significantly different, $\Delta T_p = T_p^S - T_p^R = -2.3 \pm 0.7$ K, where the range is the 95% confidence interval, and the temperatures indicate an energetic preference for *R*-3MCHO adsorption on the Cu(13,9,1)^{*R*} surface. The difference in the desorption temperatures from the straight step edges, $\Delta T_p = -0.5 \pm 0.9$, is not significantly different from zero.

The desorption of *R*-3MCHO from the $Cu(531)^{R\&S}$ surfaces is shown in figure 6. The $Cu(531)^{S}$ surface is represented by the point at the center of the stereographic triangle shown in figure 1. As such, it cannot be described as having well-defined terrace, step and kink features. Its ideal structure, as shown in figure 6, is based on the intersection of single unit cells of the (111), (110) and (100) microfacets. STM images of the Cu(531) surface reveal these features but also show that there is a significant degree of thermal roughening [27]. As shown in figure 6, TPD experiments demonstrate that there is an enantiospecific difference of $\Delta T_{\rm p} = 2.3 \pm 0.4$ K in the peak desorption temperatures for R-3MCHO desorption from the kinks on the $Cu(531)^{R\&S}$ surfaces. In contrast with the Cu(13,9,1)^{R&S} surfaces, R-3MCHO adsorption is energetically favored on the $Cu(531)^S$ surface over the $Cu(531)^R$ surface.

4. Discussion

The data compiled and presented herein may represent the most comprehensive study of the surface structure sensitivity of molecular adsorption energetics. In this regard, the choice of R-3MCHO as the probe molecule has been serendipitous; the desorption kinetics of R-3MCHO from Cu(*hkl*) surfaces reveal sensitivity to the densities of flat terrace sites, close-packed step sites, and kink sites exposed by the real structure of these surface. It is important to emphasize that the high Miller index surfaces used in the work are subject to thermal roughening and thus, the real structures of the surface are



Figure 5. *R*-3MCHO TPD spectra from the Cu(13,9,1)^{*R&S*} surfaces showing desorption from close-packed step edges and from chiral kinks. The peak desorption temperatures were determined by fitting Gaussian curves to the peaks for five independent measurements on each surface. The ranges on the peak temperatures are 95% confidence intervals estimated by $2\sigma_T^{\text{sem}}$. The peak temperatures for desorption from the chiral kink sites are enantiospecific and indicate a higher heat of adsorption on the *R*-surface than on the *S*-surface. The peak temperatures for desorption from the close-packed step edges reveals no enantiospecificity. Heating rate was 1 K s⁻¹ and the *R*-3MCHO desorption rate was monitored using m/z = 39.

not the ideal structures shown in the graphics of figures 2-4 and 6. Diffusion of atoms along step edges causes coalescence of kinks, lengthening of close-packed step edges and broadening of terraces. Simulation of these processes and STM images of real surfaces have shown that while roughening occurs, it does not eliminate the net chirality of the high Miller index surfaces [19, 24, 26, 27]. It is equally important to point out that R-3MCHO can be an invasive probe of surface structure. We have also demonstrated previously that adsorption at 300K of R-3MCHO onto Cu(221) and Cu(533) surfaces exposing close-packed step edges is sufficient to induce step edge reconstruction and the introduction of kinks into the close-packed step edges [17, 28]. Only during adsorption of *R*-3MCHO at T < 200 K, as done in this work, do the Cu(*hkl*) surfaces retain structures related to their ideal structures. Apparently, these are retained throughout the heating to desorb R-3MCHO. The second attractive feature of R-3MCHO as a probe of surface structure is the fact that it is chiral and, therefore, sensitivity to the chirality of the kink sites to which it adsorbs. This work is certainly the most comprehensive



Figure 6. *R*-3MCHO TPD spectra from the Cu(531)^{*R&S*} surfaces showing desorption from close-packed step edges and from chiral kinks. The peak desorption temperatures were determined by fitting Gaussian curves to the peaks for six independent measurements on each surface. The ranges on the peak temperatures are 95% confidence intervals estimated by $2\sigma_T^{\text{sem}}$. The peak temperatures for desorption from the chiral kink sites are enantiospecific and indicate a higher heat of adsorption on the *S*-surface than on the *R*-surface. The peak temperatures for desorption from the close-packed step edges reveals no enantiospecificity. Heating rate was 1 K s⁻¹ and the *R*-3MCHO desorption rate was monitored using m/z = 39. Reprinted with permission from [13]. Copyright 2008 Springer.



Figure 7. The stereographic triangle showing the ideal structures of the *S*-enantiomorphs of the seven chiral surfaces studied. At the upper left is a representation of the three microfacets forming the kink structures on these surfaces. Also shown are the enantiospecific heats of adsorption, $\Delta\Delta E_{des}^{S-R}$ (kJ mole⁻¹), of *R*-3MCHO on these surfaces with 95% confidence intervals. The sign of the enantiospecific desorption energies changes within the space of structures spanning the *S*-enantiomorphs.

investigation of the surface structure sensitivity of enantioselective adsorption on naturally chiral surfaces.

The data presented has allowed us to address two aspects of adsorption on stepped and kinked Cu surfaces. The first tests the convention proposed by Jenkins *et al* for classification of surfaces as flat, stepped or kinked based on the number of close-packed atomic rows presented by the surface [10]. The second is to test whether the enantiospecificity of chiral molecular adsorption is dictated purely by the convention defining the chirality of dissymmetric metal surfaces.

4.1. Surface structure classification

Jenkins et al propose that single crystal surfaces be classified as *flat* if they contain close-packed rows running in two or more directions, stepped if they have close-packed rows running only in one direction, and kinked if they do not contain any close-packed rows. The symbols representing different surfaces in the stereographic triangle of figure 1 have been chosen using this convention; open squares indicate the flat surfaces, open diamonds indicate stepped surfaces, and circles indicate kinked surfaces. Open circles indicate achiral kinked surfaces and solid circles represent the chiral kinked surfaces. Such conventions do not add much value to our understanding of structure sensitive surface chemistry unless they are correlated to physically observable properties of adsorbed molecules. The data presented above clearly demonstrates that the desorption kinetics of R-3MCHO are sensitive to surface structure: desorption from flat surfaces or terraces occurs over the temperature range 200-300 K; the peak temperatures for desorption from close-packed step edges fall in the range 335–350K; and the peak temperatures for desorption from kinks fall in the range 365-405 K. More importantly, the desorption energetics determined using the Redhead equation (table 1) correlate well with the classification scheme of Jenkins et al [10, 29]. The Cu(110) surface, in spite of being a high symmetry, low Miller index plane, is not flat and behaves much more like Cu(221) and Cu(533) than like Cu(111) or Cu(100). Similarly, the Cu(430) and Cu(410) surfaces with non-close-packed step edges behave more like the kinked surfaces than like the Cu(221) and Cu(533) surfaces.

4.2. Structure sensitive enantiospecific adsorption on Cu(hkl)^{R&S} surfaces

The TPD spectra shown in figures 5 and 6 illustrate the type of enantiospecific desorption kinetics that have been observed for *R*-3MCHO on all seven naturally chiral metal surfaces studied. The peak desorption temperatures from the kinks are dependent on the chirality of the surfaces. Table 1 lists the peak desorption temperatures for *R*-3MCHO from the chiral kinks on all 14 surfaces and the standard deviations of the 5–6 measurements on each surface. The enantiospecific differences in the mean temperature are also listed with 95% confidence intervals and reveal that *R*-3MCHO desorbs enantiospecifically from all 7 chiral surfaces. Based on these

desorption temperatures and prior evidence that desorption is a first-order process [17], we have used the Redhead equation to estimate the enantiospecificity of the desorption energetics, $\Delta \Delta E_{\text{des}}^{S-R} = \Delta E_{\text{des}}^S - \Delta E_{\text{des}}^R$ of *R*-3MCHO from the kink sites on the 7 different naturally chiral surfaces [29]. These values and 95% confidence intervals are also plotted with the structures of the surfaces in figure 7. The first point to make is that the magnitudes of the enantiospecificities are all on the order of $\left| \Delta \Delta E_{\text{des}}^{S-R} \right| \sim 1 \text{ kJ mole}^{-1}$ or ~0.3 RT at the temperature measured. To put this in perspective, an enantiospecificity of 1 kJ mole⁻¹ corresponds to an enantiospecific difference of rate constants or equilibrium constants of ~35% at 300K. This magnitude is consistent with other such measurements on naturally chiral metal surfaces: propylene oxide on Cu(643)^{*R*&S} [16], lysine on Cu(3,1,17)^{*R*&S} [20], and aspartic acid on $Cu(3,1,17)^{R\&S}$ [21]. The greatest enantiospecific desorption energy measured to date is that of methyl lactate on Cu(643)^{*R*&S}, $\Delta\Delta E_{\text{des}} \approx 4 \text{ kJ mole}^{-1}$ [30].

The adsorption energies of *R*-3MCHO on the Cu(*hkl*)^{*R&S*} surfaces are clearly sensitive to surface structure and chirality. One of the hypotheses tested by this work is whether or not the enantiospecificity is driven principally by the chirality of the surface as defined by the sense of rotation among the (1 1 1), (1 0 0) and (1 1 0) microfacets forming the kinks. In other words, is the adsorption energy of *R*-3MCHO always higher on one surface enantiomorph than the other? This is clearly demonstrated to be false. As the data in figure 7 reveal, $\Delta\Delta E_{des}^{S-R}$ is negative on the Cu(8 2 1)^{*R&S*} and Cu(13,9,1)^{*R&S*} surfaces and positive on the other five orientations studied in the course of this work. The enantio-specificity of *R*-3MCHO adsorption is dictated by surface structural features other than simply the convention used to define surface chirality.

5. Conclusions

The adsorption energetics of *R*-3MCHO on Cu(*hkl*) surfaces are sensitive to surface structure and consistent with the Jenkins *et al* categorization of surfaces as flat, stepped or kinked based on the numbers of close-packed atomic rows in the ideal surface structure. Within this convention, the Cu(110) surface is stepped and surfaces such as Cu(410) and Cu(430) that expose non-close-packed steps are kinked. On those Cu(*hkl*)^{*R&S*} surfaces that are chiral, the *R*-3MCHO desorption energetics from the kink sites are enantiospecific, $\Delta\Delta E_{des}^{S-R} \neq 0$. The sign of the enantiospecificity is not, however, determined solely by the convention based on the rotational orientation of the low Miller index microfacets that is used to assign the chirality of the surfaces.

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