Enantioselective decomposition of chiral alkyl bromides on Cu(643)$^{R\&S}$: Effects of moving the chiral center

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Abstract

The enantioselective surface chemistry of two chiral alkyl halides, S-1-bromo-2-methylbutane and R-2-bromobutane, have been compared on the naturally chiral Cu(643)$^{R\&S}$ surfaces. Temperature programmed reaction spectroscopy was used to quantify the yields of the various decomposition products during heating. A fraction of the adsorbed alkyl bromides desorb intact while the remainder decomposes by debromination to form either S-2-methyl-1-butyl or R-2-butyl groups on the surfaces. The S-2-methyl-1-butyl group then reacts by β-hydride elimination to form 2-methyl-1-butene or by hydrogenation to form 2-methylbutane. The R-2-butyl group reacts by β-hydride elimination to form butene or by hydrogenation to form butane. This surface chemistry on Cu(643)$^{R\&S}$ is not enantioselective at low coverages but is enantioselective at high coverages. In R-2-bromobutane the chiral carbon atom coincides with the debromination reaction center while the β-hydride elimination centers are achiral. In S-1-bromo-2-methylbutane the chiral carbon atom coincides with the β-hydride elimination reaction center while the center for debromination is achiral. Results show that the enantioselectivities are influenced by the surface structure to a greater extent than they are by the adsorbate structure.
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1. Introduction

The interaction of chiral molecules with a chiral environment is of interest because these enantiospecific interactions somehow lead to the evolution of homochiral life on Earth [1,2]. Practically, the importance of molecular chirality arises from the fact that the two enantiomers of a chiral molecule can have vastly different physiological impacts when ingested by living organisms. As a result, chiral compounds produced for human consumption must be produced in enantiomerically pure form by enantioselective processes such as catalysis and separation [3].

Surfaces can catalyze enantioselective chemistry, if they have chiral structures. The high Miller index surfaces of metal single crystals have structures with atomic scale kinks that are inherently chiral [4,5]. These surfaces are ideal for studying enantiospecific interactions between chiral molecules and chiral substrates because they have structures that can be well characterized. Enantiospecific adsorption on naturally chiral surfaces has been studied for nearly a decade by focusing primarily on non-reactive, enantiomerically pure, chiral molecules that adsorb and desorb reversibly on chiral Cu surfaces [6,7]. A degree of complexity has been added by studying the electrooxidation of molecules such as sugars on naturally chiral Pt electrode surfaces [8–10]. Unfortunately, the surface reaction mechanisms of these sugars and other polycyclic molecules with multiple chiral centers are not well understood; thus, the origin of the enantioselectivity observed during their reactions is not clear. Understanding the origins of enantioselective surface chemistry requires the study of reactions with well understood reaction mechanisms.

This work focuses on the surface chemistry of S-1-bromo-2-methylbutane, $BrCH_2^*CH(CH_3)CH_2CH_3$, on the

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naturally chiral Cu(643)$^{R\&S}$ surfaces. The enantioselectivity of its thermal decomposition was compared with that of R-2-bromobutane, $CH_3^*CH(Br)CH_2CH_3$, a related molecule studied in earlier work [11]. The structures of both reactants and the intermediates that they form during reactions on Cu surfaces are shown in Fig. 1. S-1-bromo-2-methylbutane and R-2-bromobutane were selected for study in this work because their reaction mechanisms on copper surfaces are well understood. During heating, some adsorbed S-1-bromo-2-methylbutane desorbs molecularly while the remainder debrominates to produce chiral S-2-methyl-1-butyl groups on the surface [12,13]. The adsorbed S-2-methyl-1-butyl groups either decompose via β-hydride elimination to produce 2-methyl-1-butene or hydrogenate to form 2-methylbutane [14–17]. The surface chemistry of R-2-bromobutane was studied previously and is quite similar to that of S-1-bromo-2-methylbutane [11]. After adsorption, some R-2-bromobutane desorbs molecularly while the remainder debrominates to form R-2-butyl groups. The R-2-butyl groups can then react by β-hydride elimination to produce butene or hydrogenate to form butane. The reactions of alkyl groups on Cu surfaces are highly selective towards the formation of olefins by β-hydride elimination and alkanes by hydrogenation and do not result in significant hydrogenolysis or complete decomposition [14–17]. The positions of these reaction centers

with respect to the chiral centers in both molecules are shown in Fig. 1. The chiral centers are illustrated with the open circles while the reaction centers are indicated with arrows. The important point to realize is that these two alkyl bromide molecules differ in the chirality of the carbon atoms at which the debromination, β-hydride elimination and hydrogenation reactions are occurring.

R-2-bromobutane and S-1-bromo-2-methylbutane are aliphatic hydrocarbons with one chiral center (Fig. 1). All of the experiments to correlate enantioselectivity with the relative positions of the chiral and reactive centers were performed on Cu(643)$^{R\&S}$. In R-2-bromobutane the chiral center is the debromination center; therefore, greater enantiospecificity is expected for debromination than for reactions occurring at non-chiral centers (i.e., β-hydride elimination). In S-1-bromo-2-methylbutane the chiral center is the β-hydride elimination center; therefore, greater enantiospecificity is expected for β-hydride elimination than for reactions occurring at non-chiral centers (i.e., debromination). Both molecular desorption and alkyl group hydrogenation exhibit measurable enantioselectivities while β-hydride elimination and debromination do not. The interesting observation is that the trends of enantioselectivity among the four reaction products are quite similar for both reactants in the sense that each exhibits the same relative enantioselectivities.
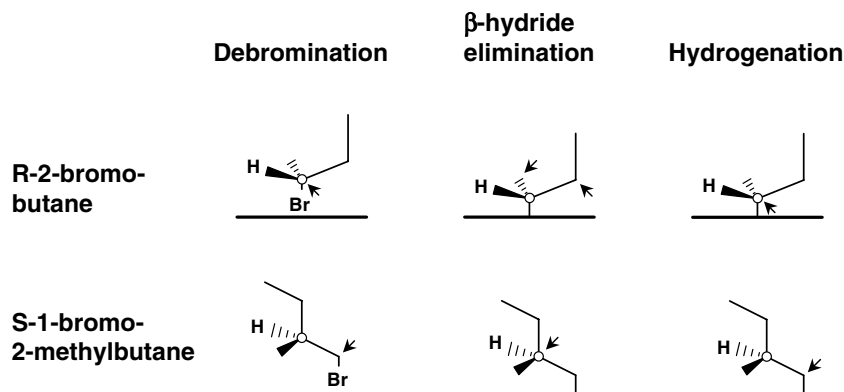

Fig. 1. Schematic structures of the chiral reactants, R-2-bromobutane and S-1-bromo-2-methylbutane, and the chiral intermediates, R-2-butyl and S-2-methylbutyl, on the Cu surface. The chiral centers are marked with the open circle. The reaction centers for debromination, β-hydride elimination and hydrogenation are marked with arrows.

Table 1
Enantioselectivities (ES) and enantiomeric excesses (ee) of desorption, debromination, β-hydride elimination, and hydrogenation during reaction of R-2-bromobutane and S-1-bromo-2-methylbutane on Cu(643)$^{R\&S}$ and R-2-bromobutane on Cu(531)$^{R\&S}$

	S-1-bromo-2-methylbutane/Cu(643)$^{R\&S}$		R-2-bromobutane/Cu(643)$^{R\&S}$		R-2-bromobutane/Cu(531)$^{R\&S}$	
	ES	ee (%)	ES	ee (%)	ES	ee (%)
Alkyl halide (desorption)	0.80 ± 0.11	11	0.61 ± 0.10	24	0.36 ± 0.13	47
Alkyl group (debromination)	1.05 ± 0.10	2.4	1.04 ± 0.07	2.0	1.18 ± 0.09	8.3
Olefin (β-hydride elimination)	1.08 ± 0.08	3.8	1.05 ± 0.06	2.4	1.20 ± 0.08	9.1
Alkane (hydrogenation)	0.73 ± 0.11	15	0.80 ± 0.11	11	1.00 ± 0.06	0.0

1.1. Enantioselectivity of alkyl halide surface reactions

In prior study of the reactions of R-2-bromobutane on the Cu(643)$^{R\&S}$ and Cu(531)$^{R\&S}$ surfaces, temperature programmed reaction spectroscopy (TPRS) was used to measure the yields of R-2-bromobutane, butene and butane desorbing from the surfaces [11]. The enantioselectivity towards a given product was defined as

$$ES_x = \frac{Y_x^{R/R}}{Y_x^{R/S}},$$

where $Y_x^{R/R}$ is the yield of product x during reaction of R-2-bromobutane on Cu$(hkl)^R$. In this definition an enantioselectivity of ES = 1 implies no enantioselectivity. ES is related to the enantiomeric excess by

$$ee_x = \left| \frac{ES_x - 1}{ES_x + 1} \right|.$$

Enantioselectivities of the four reactions of the R-2-bromobutane were then defined as follows:

$$\text{Desorption}: ES_{des} = \frac{Y_{bromobutane}^{R/R}}{Y_{bromobutane}^{R/S}}$$

$$\text{Debromination}: ES_{Br} = \frac{Y_{2\text{-butyl}}^{R/R}}{Y_{2\text{-butyl}}^{R/S}} = \frac{Y_{butene}^{R/R} + Y_{butane}^{R/R}}{Y_{butene}^{R/S} + Y_{butane}^{R/S}}$$

$$\beta\text{-Hydride elimination}: ES_{\beta H} = \frac{Y_{butene}^{R/R}}{Y_{butene}^{R/S}}$$

$$\text{Hydrogenation}: ES_H = \frac{Y_{butane}^{R/R}}{Y_{butane}^{R/S}}$$

These are the same reactions observed in this work for S-1-bromo-2-methylbutane on the Cu(643)$^{R\&S}$ surfaces; however, the reaction products desorbing from the surface in this case are S-1-bromo-2-methylbutane, 2-methyl-1-butene, and 2-methylbutane. The desorption yields of these three products have been used to define reaction enantioselectivities for desorption, debromination, β-hydride elimination and hydrogenation analogous to those defined for the reactions of R-2-bromobutane.

The enantioselectivities of the reactions of R-2-bromobutane on Cu(643)$^{R\&S}$ have been described elsewhere [11]. At low R-2-bromobutane coverage the enantioselectivity of debromination is $ES_{Br} = 1$ (not enantioselective), because ~100% of the R-2-bromobutane decomposed into R-2-butyl on both the Cu(643)$^{R\&S}$ surfaces. At low coverage the enantioselectivity of β-hydride elimination is also $ES_{\beta H} = 1$, because ~100% of the R-2-butyl decomposed into butene on both the Cu(643)$^{R\&S}$ surfaces. It is important to point out that although the reaction yields have ES = 1 there may be enantiospecific kinetics at low coverage; however, the generation of only one product does not allow detection of enantioselectivity.

At monolayer coverage of R-2-bromobutane the enantioselectivity of desorption is $ES_{des} = 0.61 \pm 0.10$, and the

enantioselectivity of debromination is $ES_{Br} = 1.04 \pm 0.07$. The enantioselectivity of β-hydride elimination is $ES_{\beta H} = 1.05 \pm 0.06$, and the enantioselectivity of hydrogenation is $ES_H = 0.80 \pm 0.11$. The fact that desorption and hydrogenation exhibit enantioselectivity indicates that R-2-bromobutane and R-2-butyl are sensitive to the chiral environment of the surface during their reactions. Table 1 shows all of the enantioselectivities and enantiomeric excesses observed for the reactions of R-2-bromobutane on Cu(643)$^{R\&S}$.

2. Experimental

Experiments were performed in an UHV chamber equipped with an Ar$^+$ gun for cleaning the copper surfaces, low energy electron diffraction (LEED) optics for determining the orientation of the Cu(643)$^{R\&S}$ surfaces, and an Extrel quadrupole mass spectrometer for TPRS measurements. The mass spectrometer was shrouded in a stainless steel housing with a 9 mm aperture to the ionizer. In the UHV chamber, the single crystal sample was mounted on a manipulator allowing xyz motion and rotation about the vertical axis of the chamber. The sample was spot-welded between two Ta wires and could be heated resistively to $T > 1000$ K. The sample could also be cooled to $T < 100$ K through mechanical contact with a liquid nitrogen reservoir. The temperature of the sample was measured using a K-type thermocouple spotwelded to the perimeter of the copper disk.

S-1-bromo-2-methylbutane was purchased from Sigma–Aldrich with a purity of >99%. Racemic 1-bromo-2-methylbutane was purchased from Pfaltz and Bauer with a purity of >97%. S-1-bromo-2-methylbutane and racemic 1-bromo-2-methylbutane were transferred to individual glass vials suited for introduction of their vapors into the UHV chamber via a leak valve. The two compounds were subjected to cycles of freezing, pumping, and thawing to remove air and other high vapor pressure contaminants. Mass spectroscopy was used to verify the purity of each sample. The purity of S-1-bromo-2-methylbutane remained suitably high; however, the purity of the racemic mixture seemed to degrade relatively rapidly as indicated by its change in color once transferred into the glass vial. Nonetheless the TPR spectra of the racemic mixture were identical on the Cu(643)$^{R\&S}$ surfaces, as they should be.

The Cu(643) sample is a single-crystal disk (12.5 mm in diameter and 2 mm thick) and was obtained from Monocrystals Co. One side of the crystal exposes the (643)^S surface, and the other side exposes the (643)^R surface. Once mounted in the chamber, the Cu(643)$^{R\&S}$ surfaces were cleaned by cycles of Ar$^+$ bombardment to remove surface contaminants. During cleaning, the ion current measured on the sample was 5 μA at an ion energy of 2.5 keV. After ion bombardment, the copper surface was annealed at 1000 K for 10 min in vacuo at a pressure of ~5 × 10^{-10} Torr. A sharp LEED pattern was the criterion used to verify surface order of Cu(643). LEED was also used

to identify the orientation of the $(643)^R$ and $(643)^S$ faces. A complete explanation of the determination of the chirality of Cu(643) using LEED has been described elsewhere [18].

After cleaning the surface, the desired adsorbate coverages were obtained by holding the $Cu(643)^{R\&S}$ surface temperature at 150 K and exposing it to the vapor of either S- or rac-1-bromo-2-methylbutane. During exposures of the $Cu(643)^{R\&S}$ surfaces to vapor, the pressure in the chamber was measured using the ion gauge. Exposures for each compound are reported in Langmuirs (1 L = 10^{-6} Torr · s) and are not corrected for ion gauge sensitivity factors. The exposures used in these experiments were either 1 L (2×10^{-8} Torr, 50 s) or 7 L (1.4×10^{-7} Torr, 50 s). The 1 L exposure generated a submonolayer coverage while the monolayer coverage was achieved by exposing the sample at 150 K to 7 L of vapor. The sample was held at 150 K during exposure to avoid multilayer formation. Higher exposures at lower temperatures resulted in the adsorption of multilayer films.

After adsorption of the desired coverages of S- or rac-1-bromo-2-methylbutane on the $Cu(643)^{R\&S}$ surfaces at 150 K, TPRS experiments were performed to study their surface chemistry. The surface was cooled to below 100 K and then moved to a position approximately 3–4 mm from the aperture of the mass spectrometer. The sample was then heated at a constant rate of 1 K/s, while using the mass spectrometer to monitor signals at m/q ratios of 43, 55, and 71. These m/q ratios are characteristic of the fragmentation patterns of S-1-bromo-2-methylbutane, 2-methyl-1-butene, and 2-methylbutane desorbing from the surface. After each TPRS experiment, the surface was cleaned by Ar^+ bombardment to remove bromine atoms that remain bound to the surface after the decomposition of S- or rac-1-bromo-2-methylbutane.

3. Results

3.1. Low coverage of S-1-bromo-2-methylbutane on $Cu(643)^{R\&S}$

The chemistry of S-1-bromo-2-methylbutane on Cu surfaces generates three gas phase products: S-1-bromo-2-methylbutane by molecular desorption, 2-methyl-1-butene from β-hydride elimination of S-2-methyl-1-butyl groups and 2-methylbutane from hydrogenation of the S-2-methyl-1-butyl groups. A low initial coverage of ~0.15 monolayers was used to study the surface chemistry of S-1-bromo-2-methylbutane on the chiral kink sites. This low coverage was produced by exposing the surface to 1 L of S-1-bromo-2-methylbutane under conditions that would saturate the monolayer, if a 7 L exposure were used. Fig. 2 shows the TPR spectra of 2-methyl-1-butene, the β-hydride elimination product, from the $Cu(643)^R$ and $Cu(643)^S$ surfaces following a 1 L exposure to S-1-bromo-2-methylbutane. The peak desorption temperature was $T_p = 288$ K and ~100% of the S-2-
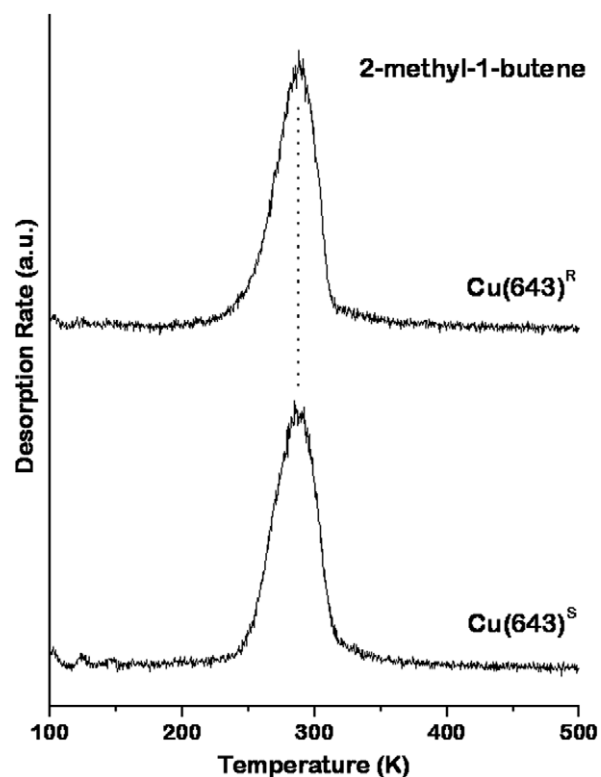

Fig. 2. TPR spectra of a low coverage of S-1-bromo-2-methylbutane on $Cu(643)^{R\&S}$. 2-Methyl-1-butene is the only product and it evolves at the same temperature on both faces of the chiral surface. The enantioselectivity is ES = 1. The evolution of the product is rate limited by desorption and so there is no enantiospecificity to the desorption kinetics.

methyl-1-butyl was converted into 2-methyl-1-butene. The TPR spectra from the two surfaces show no significant difference in either the peak desorption temperatures or the product yields. The selectivity of debromination was $S = 1$ on both surfaces and the selectivity of β-hydride elimination was $S = 1$; therefore, no enantioselectivity was detected (ES = 1). Note that the kinetics of 2-methyl-1-butene desorption from these surfaces are limited by its desorption rate constant rather than the rate constant for β-hydride elimination; thus, because 2-methyl-1-butene is achiral it is not surprising that its peak desorption temperature does not exhibit any enantioselectivity. It is also the case that because the surface chemistry of S-1-bromo-2-methylbutane yields only one product at low coverage, the product yield cannot be enantioselective. Note that this does not mean that the underlying kinetics of debromination and β-hydride elimination are not enantiospecific on the $Cu(643)^R$ and $Cu(643)^S$ surfaces. It simply means that the rate constants for debromination on the two surfaces are significantly higher than the rate constants for desorption and that the rate constants for β-hydride elimination are significantly higher than those for hydrogenation. Thus the reaction selectivities towards debromination and β-hydride elimination are both $S = 1$.

3.2. Monolayer coverage of S-1-bromo-2-methylbutane on Cu(643)$^{R\&S}$

The TPR spectra for monolayer coverages of S-1-bromo-2-methylbutane on the Cu(643)^R and Cu(643)^S surfaces (Fig. 3) are considerably different from the low coverage spectra. At monolayer coverage all reactive sites are populated with S-1-bromo-2-methylbutane. There is evidence of S-1-bromo-2-methylbutane desorption and debromination to form S-2-methyl-1-butyl groups. In addition to β-hydride elimination to yield 2-methyl-1-butene, there is evidence of S-2-methyl-1-butyl hydrogenation to 2-methylbutane. More importantly, there are subtle differences in the yields of the three products from the Cu(643)^R and Cu(643)^S surfaces. Although small, they are significant. The TPRS experiments with S-1-bromo-2-methylbutane have been repeated three times on each surface and the differences in the yields of S-1-bromo-2-methylbutane, 2-methyl-1-butene, and 2-methylbutane desorbing from the Cu(643)^R and Cu(643)^S surfaces are reproducible. In contrast, there are no significant differences between the TPR spectra of the racemic 1-bromo-2-methylbutane on

Fig. 3. TPR spectra of monolayer coverages of S-1-bromo-2-methylbutane on Cu(643)$^{R\&S}$. Some S-1-bromo-2-methylbutane desorbs during heating. The remainder reacts by debromination to produce S-2-methylbutyl groups which then react by β-hydride elimination and hydrogenation to produce 2-methyl-1-butene and 2-methylbutane. The integrated areas under these TPRS curves show that there are small, but reproducible differences in the reaction yields indicating enantioselective surface chemistry.

the Cu(643)^R and Cu(643)^S surfaces. During TPRS of S-1-bromo-2-methylbutane, more 2-methyl-1-butene is produced on Cu(643)^S than on Cu(643)^R and more 2-methylbutane is produced on Cu(643)^R than on Cu(643)^S. There is also more molecular desorption of S-1-bromo-2-methylbutane from Cu(643)^R than from Cu(643)^S. The fact that enantioselectivity is detected is a key observation and indicates that the S-1-bromo-2-methylbutane and S-1-bromo-2-methyl groups are sensitive to the chirality of the Cu(643)$^{R\&S}$ surfaces.

The peak temperatures of S-1-bromo-2-methylbutane desorption from Cu(643)^R and Cu(643)^S occur at 196 K and 206 K, respectively. Although this difference could be evidence of enantiospecific desorption from Cu(643)$^{R\&S}$, the desorption peaks are very broad and suggest that desorption is occurring from an inhomogeneous environment. It should also be pointed out that desorption occurs in competition with debromination. Thus the kinetics of the two processes are coupled and the enantioselective desorption of S-1-bromo-2-methylbutane could be a consequence of desorption rate constants that are enantiospecific or rate constants for debromination that are enantiospecific. The 2-methyl-1-butene desorption spectra are also very broad. Lastly, after the β-hydride elimination step, the appearance of 2-methyl-1-butene is rate-limited by the desorption step; thus, the kinetics of 2-methyl-1-butene desorption during the TPRS experiment cannot be used to probe enantioselectivity [11,19]. Instead, product yields were used to measure enantioselectivity.

Three sets of S-1-bromo-2-methylbutane TPR spectra were obtained on both the Cu(643)^R and the Cu(643)^S surfaces to assess the reproducibility of the surface reaction yields. The desorption and debromination yields during S-1-bromo-2-methylbutane reaction on the Cu(643)$^{R\&S}$ surfaces reveal enantioselectivities of $ES_{des} = 0.80 \pm 0.11$ and $ES_{Br} = 1.05 \pm 0.10$, respectively. The yields of β-hydride elimination and hydrogenation products during S-2-methyl-1-butyl decomposition on the Cu(643)$^{R\&S}$ surfaces reveal enantioselectivities of $ES_{\beta H} = 1.08 \pm 0.08$ and $ES_H = 0.73 \pm 0.11$, respectively. The fact that ES_{des} and ES_H are significantly different from unity indicates that the surface chemistry is enantioselective. As expected, no such enantioselectivities were observed in the reaction of racemic 1-bromo-2-methylbutane on the Cu(643)$^{R\&S}$ surfaces. Table 1 shows the enantioselectivities and enantiomeric excesses for all four reactions of S-1-bromo-2-methylbutane on Cu(643)$^{R\&S}$. This table reveals a pattern of enantioselectivity for the S-1-bromo-2-methylbutane decomposition on the Cu(643)$^{R\&S}$ surfaces that is quite similar to that previously observed for R-2-bromobutane [11]. This is quite interesting and there is no reason to expect that they should be similar. This observation must reflect some common pattern to the enantiospecificity of the underlying rate constants that lead to the enantioselective yields. Given the subtle differences in enantiospecific rate constants, the fact that the enantioselective yields are similar for the two reactants is somewhat surprising.
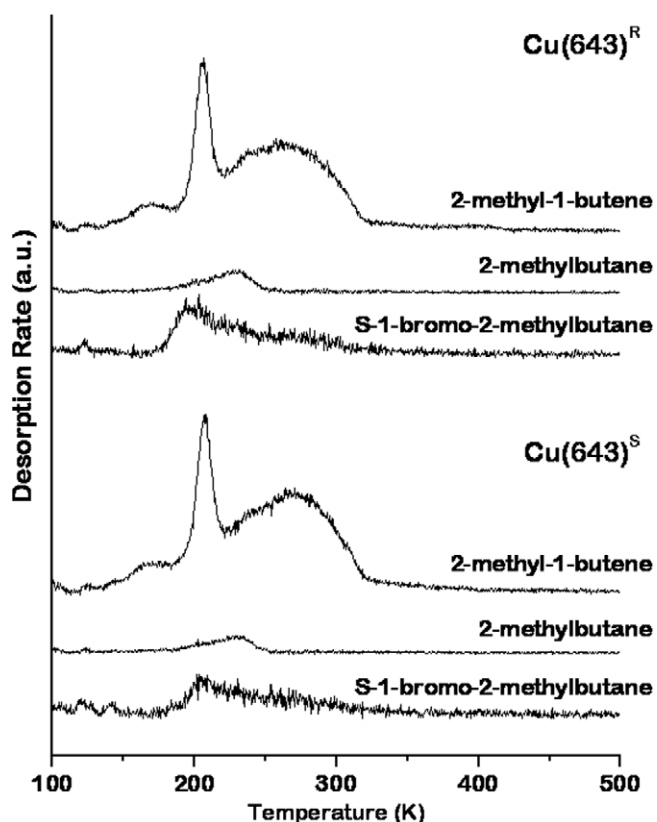
4. Discussion

The structure of chiral surfaces has been shown to clearly affect enantioselectivity in surface reactions of chiral adsorbates [11]; therefore, one would expect that the nature of the adsorbate must also influence enantioselectivity. There are many characteristics of chiral adsorbates that control reaction enantioselectivity. One important factor is the position of the chiral center relative to the position of the reaction center. As an example, a molecule with a reaction center that is separated from its chiral center by a long chain hydrocarbon is unlikely to exhibit enantioselectivity because the local environment of the reaction center is achiral. In addition to the relative positions of the chiral center and the reaction center, another important factor that probably determines enantioselectivity is the 'degree of chirality' of the chiral center. As an example, one might imagine that in many circumstances a chiral center that is attached to a methyl group, an ethyl group, and a propyl group is less chemically asymmetric than a chiral center that is attached to a methyl group, a hydroxyl group, and a fluorine atom. In general, of course, one cannot define a 'degree of chirality'. Chirality is simply a geometric property of an object. Physically, it manifests itself in chemical systems as the difference in the interaction energies of a chiral molecule or surface with the two enantiomers of a chiral probe molecule. The fact that this difference must depend on the nature of the probe precludes the rigorous definition of a general and physically meaningful 'index of chirality'.

In R-2-bromobutane the chiral center coincides with the debromination center while in S-1-bromo-2-methylbutane the chiral center is adjacent to the debromination center. In R-2-butyl the chiral center is the hydrogenation center but is adjacent to the β-hydride elimination centers. In S-2-methyl-1-butyl β-hydride elimination occurs at the chiral center while hydrogenation occurs adjacent to the chiral center. Therefore, one might expect to observe systematic differences in the enantioselectivity of surface reactions that depend on the structure of the chiral adsorbate and on the relative positions of their reaction centers and the chiral centers.

The trends in enantioselectivity among the different reaction paths for R-2-bromobutane and S-1-bromo-2-methylbutane on the Cu(643)$^{R\&S}$ surfaces are very similar. Table 1 also lists the enantioselectivities observed during the reaction of R-2-bromobutane on the Cu(531)$^{R\&S}$ surfaces [11]. In examining the enantioselectivities reported in Table 1 it appears that the enantioselectivities are correlated to surface structure to a greater extent than they are to adsorbate structure. Prior work has compared the enantioselectivity of R-2-bromobutane decomposition on Cu(643)$^{R\&S}$ surfaces with that on Cu(531)$^{R\&S}$ surfaces and clearly revealed a dependence on surface structure. Unfortunately, it is not possible to reduce the enantioselectivities observed for the four reaction products to enantiospecific rate constants for the elementary steps in the surface reactions by which they are produced. The fact that the trends among the enantioselectivities of the reactions of R-2-bromobutane and S-1-bromo-2-methylbutane are similar on the Cu(643)$^{R\&S}$ surfaces suggests that the enantioselectivities are dictated by the structure of the surface to a greater extent than they are by the internal structure of the two different adsorbates.

5. Conclusions

The reactions of R-2-bromobutane and S-1-bromo-2-methylbutane on the Cu(643)$^{R\&S}$ surfaces include desorption, debromination, β-hydride elimination and hydrogenation. The yields of these reactions indicate that their underlying kinetics are enantiospecific and thus lead to the enantioselective product yields. This represents the first comparison of the yields of enantioselective reactions on naturally chiral surfaces for which the elementary steps of the reaction mechanism are well documented. The most interesting observation is that the pattern of enantioselectivities among the products is similar for the two alkyl bromides, suggesting that the surface structure has a greater impact on enantioselectivity than the internal structures of the adsorbates.

Acknowledgement

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