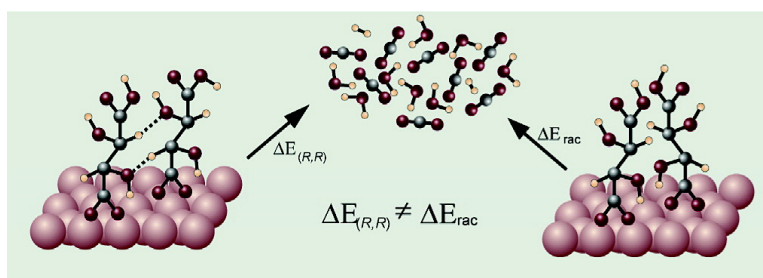


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Chiral Recognition in Surface Explosion

Bahar Behzadi, Sara Romer, Roman Fasel, and Karl-Heinz Ernst*

Swiss Federal Laboratories for Materials Research (EMPA), Molecular Surfaces Technologies-125,
Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

Received March 29, 2004; E-mail: karl-heinz.ernst@empa.ch

Molecular recognition of chiral molecules on surfaces plays an important role in processes such as enantiomeric separation of chiral compounds,¹ crystal growth,² enantiospecific sensors,³ and heterogeneous asymmetric catalysis.⁴ Despite this importance, the mechanism of chiral recognition in these surface processes is poorly understood.⁵ Stereospecific interactions with chiral kink sites on surfaces have been also observed for the oxidation of glucose on Pt(643)⁶ and for the thermally induced desorption of methyl cyclohexanone on Cu(643).⁷

Here, we report the observation that the handedness of adjacent molecules influences the thermal stability of monotartrate species on the Cu(110). By means of temperature-programmed desorption (TPD) the rapid decomposition, so-called “surface explosion”, of monotartrate has been investigated for racemic tartaric acid and the pure enantiomers.

The expression “surface explosion” was coined for an autocatalytic increase in reaction rate in thermally induced surface reactions occurring in a very narrow temperature range.⁸ This phenomenon has been observed in thermal desorption spectra of decomposition products of formate and acetate species on single-crystal surfaces⁹ and supported metal catalysts.¹⁰ The autocatalytic increase in reaction rate has been explained by metal surface sites, which serve as catalyst for a reaction that, in turn, creates new active sites. The rate equation for such process is:¹¹

$$d\theta/dt = A \cdot \theta \cdot (1 - \theta) \cdot e^{-E/RT}$$

in which θ is the molecular coverage and $(1 - \theta)$ the concentration of free reactive substrate sites. To observe “surface explosion”, the adsorbed species must be stabilized far above its regular decomposition temperature. As stabilizing preconditions causing the high activation barrier, close-packed structures in densely packed islands or monolayers have been proposed.¹⁰ Under those conditions, no surface sites are initially available, i.e., $(1 - \theta) \approx 0$. However, this does not account for the geometrical rearrangement of the molecule to react with the surface. Using molecules with mixed or pure chirality, we demonstrate here that within the close-packed lattice structure the stability of a molecule is influenced by the structure of adjacent molecules, which adds a steric component to the activation barrier.

On Cu(110), surface explosions have been recently reported for succinic acid and for (*R,R*)-tartaric acid.¹² The latter system, in particular, has been characterized in great detail by Raval and co-workers.¹³ Upon activation at 405 K, tartaric acid (TA) is adsorbed as bitartrate species, with both carboxylate groups attached to the surface and the molecular frame distorted in a zigzag sawbuck structure.¹⁴ The molecules are arranged in a lateral structure with (90,12)-periodicity.¹⁵ Depending on the enantiomer, the adsorbate lattice is aligned in opposite angles with respect to the substrate lattice, thus showing two-dimensional (2-D) enantiomorphism.¹⁶ With further increasing coverage the bitartrate is converted to

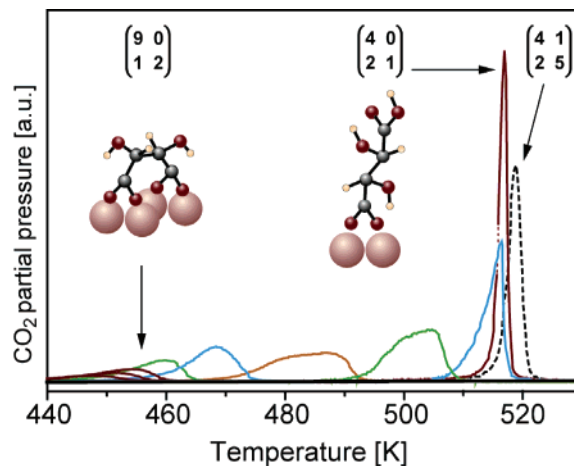


Figure 1. TPD series of (*R,R*)-TA on Cu(110). CO₂ is generated by TA decomposition and desorbs instantaneously from the surface. The decomposition signals for the bitartrate-(90,12)-, the monotartrate-(40,21)- and the monotartrate-(41,25) structures are indicated by arrows, respectively. With increasing coverage, a strong peak shift to higher temperatures is observed, while the fwhm decreases to a value of only 1.6 K for the (40,-21) structure and of 2.2 K for the (41,25) structure.

monotartrate, which is organized in a close-packed (40,21) structure followed at saturation by an enantiomorphous (41,25) structure.¹³

We present here new results for the interaction of racemic TA and the pure enantiomers with Cu(110) and focus on the different thermal stabilities of the close-packed structures prepared at 405 K. Figure 1 reviews the situation of the conversion from bitartrate to monotartrate for the (*R,R*)-enantiomer. Shown are TPD mass spectra for carbon dioxide with increasing (*R,R*)-TA surface coverage. The three lowest-coverage peaks at about 450 K represent the decomposition of the bitartrate species. The transition to the monotartrate layer is accompanied with a strong increase in desorption temperature as presented by five desorption curves with peak temperatures ranging from 460 to 510 K. Once the (40,21) structure is completed, a peak with an unprecedented small full width at half-maximum (fwhm) of only 1.6 K is observed. For the transition from (40,21) to (41,25) the peak temperature rises by 3 K, and the fwhm is increased to 2.2 K. While the higher surface density easily explains the higher decomposition temperature, the increase in fwhm is assigned to the higher heterogeneity in the (41,-25) lattice due to a mixed monomer–dimer structure.¹³

As molecular species desorbing from the surface, carbon dioxide, water, and hydrogen have been identified, all evolving at the same temperature.¹⁷ In addition, X-ray photoelectron spectroscopy (XPS) revealed a build-up of carbon on the surface, suggesting the following decomposition reaction:



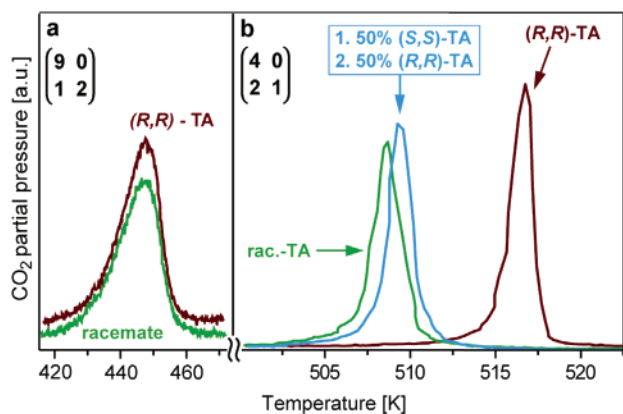


Figure 2. Comparison of CO₂ desorption signals, representative for the autocatalytic “surface explosion” reaction of TA, after exposure of the Cu(110) surface to racemic TA and (*R,R*)-TA. (a) No differences in desorption peak temperature are observed between the racemic (90,±12) and the enantiopure (90,12) structure. (b) CO₂-TPD spectra for the (40,21) monotartrate structures prepared at 405 K. The enantiopure (40,21) structure exhibits an 8 K higher decomposition peak temperature than the racemic (40,21) structure. Dosing equal amounts of the pure enantiomers leads to a (40,21) saturation structure that shows no substantial differences in decomposition temperature with respect to the racemate.

After exposure of the sample to *racemic* TA at 405 K, a superposition of the two enantiomorphous (*R,R*)-TA-(90,+12) and (*S,S*)-TA-(90,-12) diffraction patterns was observed via low-energy electron diffraction (LEED). A similar observation was explained previously for phenylglycine on Cu(110) by a lateral resolution of the enantiomers into homochiral 2-D crystallites.¹⁸ Neglecting domain boundary effects, we therefore do not expect to find differences in the decomposition kinetics between racemic mixture and enantiopure structures. Comparing the respective TPD signals confirms this conclusion (Figure 2a). In contrast to the pure enantiomers, further exposure to racemic TA leads only to the formation of a (40,21) LEED pattern. The surface coverage for the enantiopure (41,25) structure, as determined via XPS and TPD, was found to be about 10% higher than the racemic and enantiopure (40,21) structures.¹⁹ With lateral enantioseparation involved, however, the formation of the two enantiomorphous (±41,±25) structures must be expected for the racemate, leading to a higher coverage than $\theta = 0.25$.

Desorption peaks from (40,21)-monotartrate structures are shown in Figure 2b. Clearly, the pure enantiomer shows a higher decomposition temperature than the racemate. The activation energies for the reactions, as determined by systematic heating rate variation,²⁰ are 142 ± 3 and 162 ± 3 kJ/mol for racemate and (*R,R*)-TA, respectively.²¹ The comparison of the equal-coverage (40,21) structures shows an 8 K higher decomposition temperature for monotartrate in the pure enantiomer lattice. Again, this difference can only be explained by formation of a heterochiral structure of the racemate on the surface. Since identical chemical species are present on the surface and because of the identical 2-D lattice structures at this coverage, the observed differences for racemate and pure enantiomers must be assigned to stereochemistry. That is, the handedness of adjacent molecules has an influence on the stability of a monotartrate species.

To start the decomposition reaction, either an OH- or the COOH-group must be brought into contact with the surface. Besides the availability of reactive surface sites, the local rearrangement or the unhooking of a single monotartrate from the lattice comes into play.

The higher activation barrier for breaking down the close-packed structure, therefore, stems from lateral interactions between the molecules. It has been pointed out recently that the formation of 2-D enantiomorphous bitartrate structures is mediated by substrate rather than governed by intermolecular hydrogen bonds.^{12,14b} Although racemate and pure enantiomer form the same monotartrate lattice structure, i.e., the substrate geometry governs the self-assembly, the formation of intermolecular hydrogen bonds, however, is influenced by the handedness of the molecules and can still have an influence on the lattice stability. In particular, long-range hydrogen-bonded chain structures cannot be established within the (40,21) heterochiral structure as easily as in the respective homochiral arrangement. The observed higher stability for the enantiopure lattice is in contrast to that of 3-D tartaric acid crystals and to most of the other chiral 3-D crystals.²² However, it agrees with the fact that at lower dimensionality homochirality is favored, as observed for the self-assembly of biomolecules via hydrogen bonds.

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Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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