

Critical Influence of Adsorption Geometry in the Heterogeneous Epoxidation of “Allylic” Alkenes: Structure and Reactivity of Three Phenylpropene Isomers on Cu(111)

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Abstract: It has long been conjectured that the difficulty of heterogeneously epoxidizing higher alkenes such as propene is due to the presence in the molecule of “allylic” H atoms that are readily stripped off by the oxygenated surface of the metal catalyst resulting in combustion. Here, taking advantage of the intrinsically higher epoxidation selectivity of Cu over Ag under vacuum conditions, we have used three phenylpropene structural isomers to examine the correlation between adsorption geometry and oxidation chemistry. It is found that under comparable conditions α -methylstyrene, *trans*-methylstyrene, and allylbenzene behave very differently on the oxygenated Cu(111) surface: the first undergoes extensive epoxidation accompanied by relatively little decomposition of the alkene; the second leads to some epoxide formation and extensive alkene decomposition; and the third is almost inert with respect to both reaction pathways. This reactive behavior is understandable in terms of the corresponding molecular conformations determined by near-edge X-ray absorption fine structure spectroscopy and density functional theory calculations. The proximity to the surface of the C=C function and of the allylic H atoms is critically important in determining reaction selectivity. This demonstrates the importance of adsorption geometry and confirms that allylic H stripping is indeed a key process that limits epoxidation selectivity in such cases.

Introduction

Heterogeneously catalyzed alkene epoxidation is academically interesting and technically important: mechanistic issues are still debated, and epoxides are valuable and versatile industrial products that are produced globally on a large scale. In the case of *ethene*, catalysis by silver represents the state of the art—under industrial conditions selectivities of ~80% are achieved and there is a broad agreement about the essential features of the reaction mechanism.¹ The direct heterogeneous epoxidation of *propene* by oxygen would be an even more attractive process from an industrial point of view. The epoxide is a very valuable material that is currently made by indirect homogeneous chemical routes that are inefficient in terms of atom economy and far from environmentally benign.² In this case Ag is ineffective, delivering epoxidation selectivities of only ~5%.³ It is generally thought that this behavior is due to the presence of allylic hydrogen atoms that are readily stripped off by the oxygenated metal surface to yield a stable adsorbed allylic species, thus precluding epoxidation and leading to deep

oxidation ($\rightarrow\text{CO}_2 + \text{H}_2\text{O}$). Though intuitively reasonable, this hypothesis remains to be established.

In principle, spectroscopic and reaction studies carried out on well-defined surfaces under ultrahigh vacuum (UHV) conditions offer a means of examining this problem at a fundamental level. However, it is not possible to study the adsorption and subsequent oxidation of propene itself on relevant metal single-crystal surfaces under vacuum conditions because its adsorption enthalpy is too low—the molecule desorbs before it can react. This problem can be circumvented by using an appropriate model alkene that is more strongly adsorbed, but mimics the molecule of interest. Thus we have validated the use of styrene as a mimic for ethene,^{4,5} the phenyl group serving to anchor the molecule to silver surfaces sufficiently so as to permit detailed examination of structural and reactive properties under vacuum conditions. By use of this approach, we have also shown that with *nonallylic* alkenes metallic Cu is much more selective toward epoxidation than metallic Ag.^{6–8} Here, combining

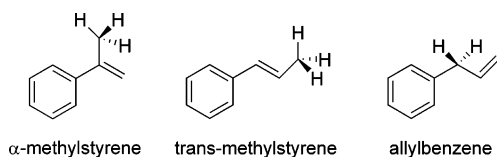
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Chart 1. α -MS, TMS, and AB Are Structural Isomers that Contain Allylic H Atoms, as Shown^a



^a Abstraction of these by adsorbed O could trigger combustion. O insertion into the olefinic C=C would result in the corresponding epoxide. Thus the relative proximity of these functionalities to the oxygenated surface could strongly affect reactive behavior.

experiment and theory, we examine the adsorption geometry and oxidation chemistry of three propene analogues on Cu(111) in order to establish whether allylic hydrogen atoms are indeed critically important in determining their epoxidation behavior.

The structural isomers α -methylstyrene (α -MS), *trans*-methylstyrene (TMS), and allylbenzene (AB) are phenylpropenes—all three contain allylic H atoms. However their adsorption geometries are likely to be different: especially in regard to the dispositions of the allylic hydrogens and the C=C function with respect to the surface (see Chart 1). We find that Cu is very effective in the epoxidation of α -MS, somewhat effective in the case of TMS, and almost totally inert toward AB. This correlates very well with respective adsorption geometries deduced from near-edge X-ray absorption fine structure (NEXAFS) experiments and density functional theory (DFT) calculations.

Experimental Methods

Temperature programmed reaction (TPR) studies were performed in a UHV chamber operated at a base pressure of $\sim 10^{-10}$ mbar; this apparatus and the methods used for sample mounting and manipulation are described elsewhere.⁹ Before each experiment, the Cu(111) sample was cleaned by Ar⁺ sputtering and annealed to 800 K, surface quality being checked by Auger and low-energy electron diffraction (LEED). TPR spectra were acquired with a ramp rate of 8 K s⁻¹, with the ionizer of the quadrupole mass spectrometer located ~ 1 cm from the crystal front face.

X-ray photoelectron spectroscopy (XPS) and NEXAFS were carried out at the SuperESCA beamline at Trieste, Italy. The degree of linear polarization of the photons was 0.99, and the photon energy was calibrated (± 0.2 eV) by the position of C *K*-edge dip in the monochromator output. XPS and NEXAFS spectra were collected using a double-pass 32-channel hemispherical electron analyzer. The angle between the entrance lens of the analyzer and the incoming photon beam was 70° in the horizontal plane. Further experimental details are given elsewhere.⁹ Methods employed for sampling cleaning and gas dosing were the same as those used in Cambridge. Coverages determined by XPS are specified in monolayers (ML) referred to the number density of metal atoms on the Cu(111) surface.

Theoretical Methods

The electronic structures and equilibrium geometries of the three molecules adsorbed on Cu(111) were calculated by density functional theory using a two-layer Cu₇₃(37,36) substrate cluster of bulk geometry shown in Figure 1. All numerical calculations are performed with the computer code StoBe¹⁰ together with the gradient corrected RPBE exchange/correlation functional.^{11,12} The atomic Gaussian basis sets used

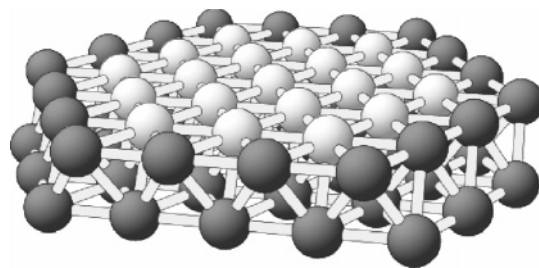


Figure 1. Cu₇₃(37,36) cluster simulating the Cu(111) surface. Light gray balls are copper atoms described by all-electron basis sets; dark gray balls are copper atoms described by ECPs.

for the substrate cluster are all-electron DZVP type¹³ for the 19 inner copper atoms, marked in light gray in Figure 1, while effective core potentials (ECP) describing the Cu 1s–3d core together with appropriate 4s,p valence bases¹⁴ are applied for all other copper atoms, marked in dark gray in Figure 1. The carbon basis sets are all-electron triple- ζ valence plus polarization (TZVP)¹⁵ type in a [4s, 3p] contraction with one added d function while hydrogen basis sets are primitive (5s) augmented with one p function and contracted to [3s, 1p].¹⁶

The equilibrium geometries of the three molecular substrates, TMS, α -MS, and AB, are found to be quite similar to those of the corresponding free gas-phase molecules with average values of the adsorbate–substrate distances of about 3 Å and adsorption energies of 0.45 eV for TMS, 0.38 eV for α -MS, and 0.29 eV for AB, from total energy differences of the clusters. These values are inline with the desorption temperature maximum observed in the TPD spectra for the corresponding molecules: 303 K for TMS, 292 K for α -MS, and 247 K for AB. Furthermore, they confirm the overall weak binding of the adsorbates. Further details are given elsewhere.¹⁷

In subsequent StoBe calculations the geometry-optimized structures are used to evaluate theoretical angle-dependent NEXAFS spectra for C1s core excitation originating at all nonequivalent carbon centers of the adsorbate molecules. Here the complete excitation spectrum of each molecule is determined using Slater's transition state (TS) method^{18,19} and considering electronic dipole transitions. In these calculations the orbital basis of the corresponding ionization center is of all-electron IGLO-III quality²⁰ yielding an improved representation of relaxation effects in the inner atomic shells. For the remaining carbon centers, effective core potentials (ECPs)¹⁴ describing the C 1s core and appropriate valence basis sets are applied. (The use of ECPs simplifies the identification of the core hole orbital while it has only negligible effects on the computed excitation spectrum.²¹) Finally, a large diffuse even-tempered [19s, 19p, 19d] basis set,²² located at the excited carbon center, is included in the transition state calculations accounting for unbound resonance wave functions within the core electron region (double basis set technique²²).

The DFT TS calculations assume a frozen molecular ion density and thus neglect electronic relaxation on the molecular ion core upon adding the excited electron. This relaxation is accounted for in an

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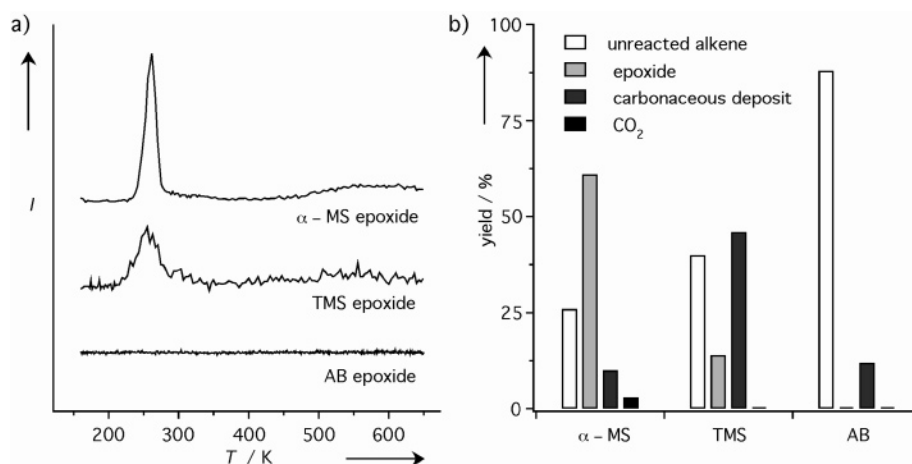


Figure 2. (a) TPR spectra showing formation of phenylpropene epoxides resulting from reaction between ~ 0.1 ML of α -MS, TMS, and ~ 0.07 O_a ML on Cu(111). (b) Percentage of the initially adsorbed alkene converting to each of the various gaseous species and to hydrocarbonaceous residue. α -MS and TMS form the respective epoxides, whereas AB does not. Moreover, α -MS undergoes much more epoxidation than TMS, while most of the AB desorbs without reaction.

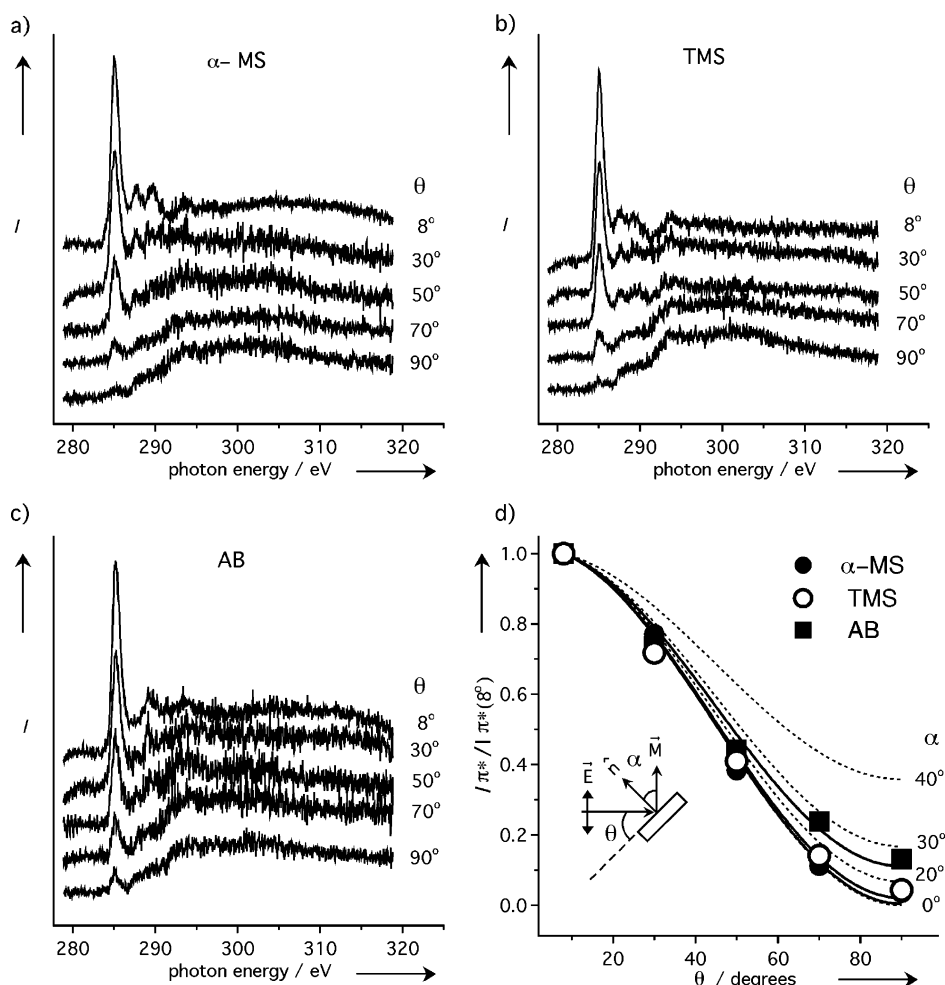


Figure 3. Normalized carbon K-edge NEXAFS spectra as a function of photon incidence angle ($\theta = 8, 30, 50, 70,$ and 90°) for 0.05 ML of (a) α -MS, (b) TMS, and (c) AB adsorbed on Cu(111) at 175 K. Figure 2d data points are C1s $\rightarrow \pi^*$ resonance intensities normalized to that at grazing incidence ($\theta = 8^\circ$) as a function of photon incidence angle. Curves show the fit to the Stohr model²⁶ for different values of tilt angle (α).

approximate way by correcting all excitation energies by the difference of the ionization potential evaluated with the TS method and the corresponding value from Δ Kohn–Sham calculations. Further, the excitation spectrum is corrected by a rigid shift of 0.2 eV to higher energies to account for relativistic effects contributing to core excitation.²³ The improved discrete excitation spectrum is then subject to a

Gaussian convolution with an energy-dependent broadening to arrive at a theoretical spectrum to be compared with NEXAFS experiments. In the energy region below ionization threshold the broadening (full

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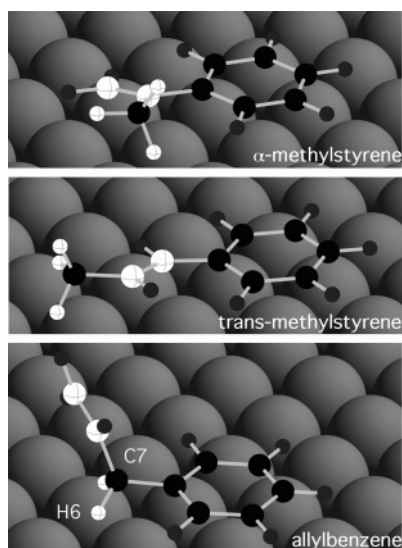


Figure 4. Molecular conformation of α -MS, TMS, and AB adsorbed on Cu(111) as determined by our DFT calculations. Vinyl group and allylic hydrogen atoms are shown in white. α -MS and TMS adopt a “flat” geometry with the vinyl and phenyl groups coplanar, whereas AB lies with the phenyl group parallel to the surface and the vinyl group directed away from the surface. Furthermore, allylic hydrogen atoms in TMS are closer to the surface than in α -MS. The disposition of the C=C bond and the allylic H atoms with respect to the copper surface determine the selectivity of the surface chemical reaction.

width at half-maximum, fwhm) was set to 0.5 eV while a linear increase up to a width of 4.5 eV was assumed for higher energies, as is common practice in the analysis of experimental NEXAFS spectra.^{24,25}

The theoretical angle-dependent NEXAFS spectra of the adsorbate molecules are compared with those of the corresponding free gas phase molecules fixed at the adsorbate orientation. For all three molecules, this comparison yields quite similar spectra with only small differences in the transition intensities which confirms the above-mentioned weak adsorbate–substrate coupling.¹⁷

Results and Discussion

Figure 2a shows TPR spectra corresponding to formation of the three phenylpropene epoxides which result from adsorption of ~ 0.1 ML alkene and 0.07 O_a ML at 150 K, followed by heating. The corresponding yields of products other than H_2O (detected but not quantifiable) are shown in Figure 2b. All relevant TPR spectra and the method used for identification of the partial oxidation products are given in the supplementary information. Clearly, α -MS exhibits the highest overall activity and selectivity toward epoxidation; TMS comes next, with AB almost inert ($\sim 10\%$ decomposition and a little water). The same pattern of behavior was found over a range of alkene and oxygen coverages.

Adsorption geometries of the isomers were determined by NEXAFS. Figure 3 shows step edge normalized carbon K-edge NEXAFS spectra as a function of photon incidence angle (θ) for ~ 0.05 ML of (a) α -MS, (b) TMS, and (c) AB at 175 K. The principal feature of interest is the resonance at 285.2 eV which, on the basis of DFT calculations, can be assigned to overlapping $C1s \rightarrow \pi^*$ transitions associated with the phenyl and vinyl groups. The intensity variation of this resonance with

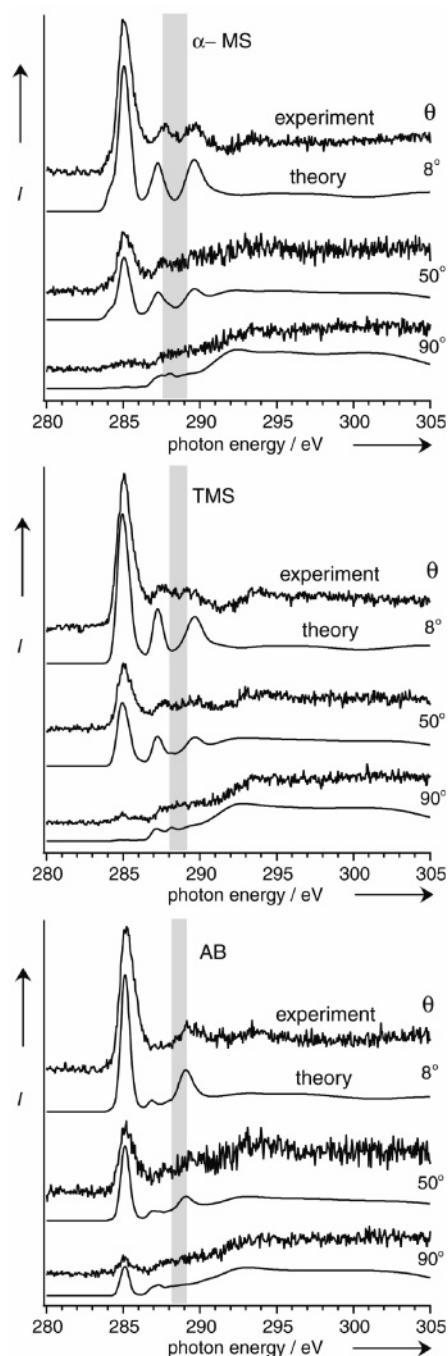


Figure 5. Comparison of experimental and theoretical NEXAFS spectra of adsorbed α -MS, TMS, and AB as a function of photon incidence angle ($\theta = 8, 50,$ and 90°). Theoretical spectra are obtained from TS calculations and shifted to lower energy (by 1.37 eV (α -MS)/1.38 eV (TMS)/1.49 eV (AB)) to account for ionization potential relaxation and relativistic corrections; for details see text. The gray region indicates the range of ionization potentials of the nonequivalent carbon atoms.

photon incidence angle is determined by the relevant selection rule²⁶ and provides information about the molecular tilt angle (α) with respect to the surface. By use of standard procedures,²⁶ we calculate the expected $I_{\pi^*}(\theta)$ dependence for different values of α and the best fits to experiment (Figure 3d, full lines) yield apparent tilt angles of 5° for α -MS, 10° for TMS, and 25° for AB. Within the experimental error, these values were unchanged for a range of alkene coverages and were also unaffected by

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the presence of coadsorbed oxygen. It should be noted that a full geometric conformation of the three adsorbate molecules cannot be obtained from the present experimental procedure based on the Stöhr method.²⁶ The latter assumes a completely planar adsorbate which holds approximately for α -MS and TMS but is less appropriate for AB.

Within the above constraint, the molecular conformations derived from experiment are fully consistent with DFT geometry optimizations, which yield the equilibrium structures shown in Figure 4. The corresponding adsorption geometries are close to those of the free molecules indicating relatively weak binding with the surface and consistent with the calculated adsorption energies of ~ 0.4 eV. Figure 5 shows theoretical NEXAFS spectra for α -MS, TMS, and AB calculated for the optimized adsorption geometry.¹⁷ Corresponding experimental spectra are also shown and yield excellent agreement which provides strong confirmation of the calculated adsorption geometry. These structures (Figure 4) provide clear insight into the striking differences in reactive behavior exhibited by the three isomers. Both α -MS and TMS adopt an essentially planar geometry with the vinyl group and the allylic H atoms close to the surface. Thus, *both* functionalities are susceptible to attack by adsorbed oxygen leading to epoxidation and decomposition, respectively, in accord with experiment. However, α -MS has the olefinic C=C bond closest to the surface, thus accounting for its highest-of-all epoxidation selectivity, again in excellent agreement with observation. Moreover, the allylic H atoms in TMS are closer to the surface (~ 0.13 Å) than they are in α -MS, an effect that operates in the same direction: TMS is more susceptible to allylic H abstraction than α -MS. The inert behavior of AB nicely completes the picture. Here, the C=C group is directed away from the surface, which suppresses epoxidation. At the same time H abstraction at C7 is inhibited because the resulting allylic

species would correspond to H6 being “buried” in the copper surface—a constraint that does not apply to the other two isomers.

Conclusions

In summary, our combined experimental and theoretical study gives insight into key aspects of the mechanism of higher alkene epoxidation on Cu, as follows.

(1) NEXAFS and DFT calculations show that the structural isomers α -MS, TMS, and AB adopt distinctly different adsorption geometries on Cu(111). Confidence in these findings is enhanced by the excellent agreement between the experimental and calculated NEXAFS spectra.

(2) The very different oxidation chemistry of the three molecules correlates with their conformation on the metal surface. The proximity to the surface of the C=C function and of the allylic H atoms is critically important in determining reaction selectivity.

(3) The observed pattern of behavior demonstrates the importance of adsorption geometry and confirms that allylic H stripping is indeed a key process that limits epoxidation selectivity in such cases.

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Supporting Information Available: All relevant TPR spectra and the method used for identification of the partial oxidation products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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