Available online at www.sciencedirect.com
ScienceDirect
Surface Science 601 (2007) 1409–1418
SURFACE SCIENCE
www.elsevier.com/locate/susc

The adsorption of 1,3-butadiene on Ag(1 1 1): A TPD/IRAS study and importance of lateral interactions

Jan Hrbek [a,*], Zhipeng Chang [b], Friedrich M. Hoffmann [c]

[a] *Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA*
[b] *Department of Chemistry, University of York, Heslington, York YO10 5DD, UK*
[c] *Department of Science, BMCC-CUNY, 199 Chambers St, New York, NY 10007-1097, USA*

Received 26 July 2006; accepted for publication 8 January 2007
Available online 12 January 2007

Abstract

Temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS) have been used to study the adsorption, desorption, molecular orientation and conformation of 1,3-butadiene on Ag(1 1 1) at 80 K. Butadiene adsorbs weakly as an s-trans conformer with the first layer oriented parallel to the silver surface and desorbs without decomposition. A very narrow line shape of the out-of-plane modes at low submonolayer coverage indicates molecular ordering within the diluted adsorbed layer, presumably through weak π-bonding interaction with the surface and intermolecular repulsive interaction. Compression within the first layer at coverages above 0.5 ML is driven by repulsive interaction as seen in both TPD and IRAS data. The IR intensity rollover and peak broadening, together with a significant shift in the TPD peak to lower temperature, indicate a reorientation of the butadiene molecule. Adsorption in the second- and multilayer is characterized by distinct IR frequency shifts and crystal field splitting effects similar to those reported for solid butadiene.

Keywords: 1,3-butadiene; Ag(1 1 1); Infrared reflection absorption spectroscopy; Adsorption; Temperature programmed desorption

---

1. Introduction

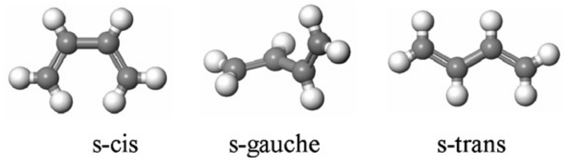
Besides its industrial importance, 1,3-butadiene (BD) is the simplest conjugated hydrocarbon and as such it provides a model to measure and interpret spectroscopic and thermodynamic data for this group of hydrocarbons [1,2]. Furthermore, fundamental details of the interaction of unsaturated bonds with metal surfaces are crucial for a better understanding of its surface mediated chemical transformations. BD has three isomers, two planar ones, s-trans (180°) and s-cis (0°), and a non-planar s-gauche (90°), models of which are shown in Scheme 1. These isomers are described by their internal bond rotation angle around the C_2–C_3 axis (0–180°). Matrix isolation studies have shown that the most stable of these conformers is the s-trans, but evidence for a second higher energy conformer (s-cis or s-gauche) has been found with thermal trapping experiments [3,4]. Gas phase data showed that a low energy s-trans conformer constitutes a majority species with a molar fraction of 0.96 at 281 K and 0.89 at 360 K [2]. Estimates for the enthalpy difference between conformers are 3.9 kcal/mol between s-cis and s-gauche and 6.7 kcal/mol between s-trans and s-gauche [5–7].

The adsorption of BD has been investigated on various metal surfaces, and distinctly different adsorption behavior was found between noble and transition metals. While butadiene molecules are strongly perturbed and dissociate at higher temperature on Pt(1 1 1) and Pd(1 1 1) [8], the formation of a $(CH)_4$ metallacycle was proposed for adsorption on Ru(0 0 0 1) [9]. In contrast, adsorption on noble metal surfaces is relatively weak. Coulman et al. [10] demonstrated in a NEXAFS study of BD adsorbed on Ag(1 1 0)

---

[*] Corresponding author. Tel.: +1 631 344 4344; fax: +1 631 344 5815.
E-mail address: hrbek@bnl.gov (J. Hrbek).

0039-6028/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2007.01.005



Scheme 1.

that at submonolayer coverage the molecule is adsorbed intact and is oriented nearly flat on the surface. Similar behavior was reported for BD adsorbed on Au(111) and Ag(111) based on an IRAS study by Osaka et al. [11]. At submonolayer coverage, the authors observed a weakly π-bonded trans conformer with the molecule adsorbed in two different adsorption sites. Adsorption in the first state, with the molecule oriented parallel to the surface, was predominantly observed at low temperature (25–30 K). Upon increasing the temperature to 90 K, the first state partially converted to a second state with a characteristic tilting of the molecular plane. As a possible mechanism for this conversion, the authors proposed that the increased surface mobility at elevated temperatures resulted in a transition from terrace sites to step and/or kink sites, although the exact nature of the adsorption site was not known [11]. Müslehiddinoğlu and Vannice [12] studied adsorption of BD on Ag/α-Al_2O_3 catalysts using diffuse reflectance Fourier transform infrared spectroscopy and identified 1,2-butadiene and crotonaldehyde in addition to weakly bonded BD.

Understanding the nature of this transition between the two adsorption states and the reorientation of the molecule is important, since this behavior appears to be of a more general nature for alkenes adsorbed on silver and other noble metals. Reorientation of the molecule at high coverage has been also observed for ethylene adsorbed on Ag(100) in an earlier IRAS study by Slater et al. [13], who proposed that at higher coverage repulsive short-range intermolecular interactions resulted in steric crowding forcing the rotation of the molecular plane towards the surface normal. The role of repulsive interactions and their effect on the adsorption of alkenes on Ag(110) has been studied in detail by Pawela-Crew and Madix [14–16]. These authors conclude that adsorbed alkanes and alkenes show substantial differences with regard to the intermolecular interactions among molecules. Alkenes display moderately strong intermolecular repulsion, while for alkanes the interaction is weakly attractive. While the repulsive behavior of various alkenes is clearly observed in thermal desorption, leading to a shift in the thermal desorption peak temperature with increasing coverage, surprisingly the IR spectra show only moderate frequency shifts as the surface coverage is increased [13,16].

In order to address these issues and the effect of intermolecular repulsion on adsorbed BD, we have investigated the adsorption of BD on Ag(111) with temperature programmed desorption and high resolution FT-IRAS. Temperature-dependent FT-IRAS measurements are aimed to investigate the effect of intermolecular repulsion at elevated substrate temperature close to desorption and thus allow direct comparison of TPD and IRAS measurements.

2. Experimental methods

Experiments were performed in an UHV chamber, which contained facilities for Fourier transform infrared reflection absorption spectroscopy (FT-IRAS), low energy electron diffraction (LEED), temperature programmed desorption (TPD) and Auger electron spectroscopy (AES). FT-IRAS was performed using a vacuum Nicolet 20F Interferometer utilizing synchrotron radiation from the U4-IR beamline at the NSLS at Brookhaven National Laboratory (spectral range from 50 to 4000 cm^{-1}). The IR light was focused at an angle of incidence of 85° onto a Ag(111) single crystal [17,18]. Infrared spectra could be obtained with different beamsplitters, IR transmitting windows, and liquid helium cooled detectors. In the present experiments two set-ups were used for the mid-IR and far-IR range, respectively: A liquid helium cooled CuGe detector in combination with a KBr or Si beamsplitter for the mid-IR range from 320 to 2500 cm^{-1}, and a liquid helium cooled boron doped Si bolometer in combination with a Si beamsplitter for the IR range from 180 to 650 cm^{-1}. The spectra reported here were obtained at resolutions of 0.25–4 cm^{-1} by typically co-adding 500 scans.

The Ag(111) single crystal sample was mounted on a manipulator capable of resistive heating to 1200 K and cooling to 80 K. The sample was a disk (∼12 mm in diameter and 2 mm thick) held tightly using a Ta loop imbedded in a groove machined around the crystal edge. Two Ta filaments spot welded to the Ta loop and attached directly to the manipulator feedthrough were used for both mechanical support and heating/cooling. Temperature was measured by a type C thermocouple spot welded to the Ta loop. The Ag(111) sample was cleaned by cycles of alternate Ar-ion sputtering and annealing to ∼700 K until no impurities were detected by Auger electron spectroscopy. BD was obtained from Phillips Petroleum (99.85 mol%) and analyzed before its use in experiments by MS/GC for gas cleanliness. Exposures of the Ag(111) sample to BD were made through backfilling the UHV chamber. Gas cleanliness in the UHV chamber was verified by a UTI 100C mass spectrometer that was also used for thermal desorption experiments.

Thermal desorption data were obtained in a second UHV chamber equipped with a quadrupole mass spectrometer, LEED and AES spectrometer. The mass spectrometer was interfaced to a PC-based data acquisition system allowing simultaneous collection of up to 10 masses. BD desorption spectra were collected at a heating rate of 2 K/s, monitoring several masses including *m*/*e* 39, one of the main fragments. In addition, thermal desorption spectra were also obtained on the FT-IRAS chamber for reference purposes. In order to determine the surface coverage of the corresponding IR spectrum, desorption spec-