nouilli numbers:[17] it is close to 1 for small x and close to x for large values of x itself. Consequently, the integral is approximately x for small x and $\approx x^2/2$ for large x.

As far as the standard changes of thermodynamic potentials upon adsorption are concerned, from eq A4 and A17 it results

$$T\Delta S° = RT \ln K_2 - X_2 + RT \qquad (A23)$$

This equation can be given a simple interpretation. $-X_2$

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(17) *Handbook of Mathematical Functions*: Abramowitz, M., Stegun, I. A., Eds.; Dover Publications Inc.: New York, 1972; p 804.

$+ RT$ is $\Delta H°$ at zero coverage; $\Delta S°$ is the standard entropy change at any coverage, including $\Theta \approx 0$. It results that

$$RT \ln K_2 = -\Delta F° \qquad (A24)$$

i.e., the standard free enthalpy change at zero coverage is simply related to K_2, which actually acts as the equilibrium constant for the adsorption at vanishing coverage.

Registry No. CO, 630-08-0; TiO$_2$, 13463-67-7.

Adsorption of Butadiene on Mo(100) below Room Temperature

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Ultraviolet photoelectron spectroscopy indicates that butadiene adsorbs molecularly onto Mo(100) at 120–150 K. The occupied molecular orbitals are only minimally perturbed on adsorption, and work function measurements indicate that bonding to the surface is by electron donation from the metal to the adsorbed butadiene. Both near-edge X-ray absorption fine-structure measurements and angle-resolved photoelectron spectroscopy indicate that the molecular plane of butadiene is oriented at ~40° to the metal surface. Warming a butadiene-covered surface to 200 K results in the thermal transformation of chemisorbed butadiene to a different surface species exhibiting a photoelectron spectrum that corresponds well to that of gas-phase *trans*-2-butene. This observation is in accord with theoretical predictions that suggest that the middle C–C bond of butadiene should be strengthened relative to the terminal C–C bonds on chemisorption.

1. Introduction

The chemisorption of C$_4$ hydrocarbons on well-characterized surfaces has received scant attention in the literature. The catalytic chemistry of olefins over molybdenum has, however, been examined in somewhat more detail, primarily because of its effectiveness as a catalyst for olefin metathesis.[1-3]

In contrast to tungsten, single-crystal studies of the chemisorption of small hydrocarbons on molybdenum are rather rare. The majority of the work has focused on the decomposition of thiophene[4-9] and sulfur-containing molecules.[10-12] A recent study has reported the effect of coadsorbed sulfur or carbon on the reactivity of a range of C$_4$ hydrocarbons.[13] More recently, theoretical calcu-

lations by Baetzold have compared the chemistry of 1,3-butadiene (subsequently referred to as just butadiene) with that of ethylene.[14] It is suggested in this work that the butadiene terminal carbon–carbon bonds are considerably weakened on chemisorption while the middle carbon–carbon bond is at the same time considerably strengthened. The study also indicates that bonding to a metal surface, particularly when the metal is near the center of the periodic table, is by donation into the π antibonding orbitals, leaving the adsorbed molecule with a residual negative charge. These conjectures are borne out experimentally by the data presented below.

Finally, Baetzold calculates an equilibrium geometry in which the molecules lie *parallel* to the (111) face of an fcc metal. The angle-resolved photoelectron spectroscopic and NEXAFS data presented below indicate that on Mo(100) the molecular plane of butadiene is, in fact, tilted with respect to the surface.

2. Experimental Section

The angle-resolved photoelectron spectroscopy and near-edge X-ray absorption fine-structure (NEXAFS) experiments were carried out at the Brookhaven National Laboratory on the National Synchrotron Light Source on beam line U14A. The ap-

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(13) Kelley, D. G.; Salmeron, M.; Somorjai, G. A. *Surf. Sci.* **1986**, *175*, 465.
(14) Baetzold, R. *Langmuir* **1987**, *3*, 189.

paratus and analysis protocol used for these experiments have been described in detail elsewhere.[15] Briefly, however, absorption cross sections in NEXAFS were measured at the carbon edge as a function of photon energy by detecting the carbon KLL Auger electrons emitted due to the decay of the C 1s core hole. To preclude possible interference due to photoemission from the substrate d-bands, the resolution of the cylindrical mirror analyzer (CMA) that was used for Auger detection was degraded by using a modulation amplitude of 30 V. Auger detection yielded spectra essentially identical with spectra obtained by measuring the total current to ground. This latter method of measuring absorption cross section is inherently less sensitive than Auger detection but served to confirm that there was no interference from photoelectron peaks.

The raw absorbance data were normalized to the incident photon flux and the final NEXAFS spectra obtained by ratioing the spectrum of the adsorbate-covered surface to that of a clean surface taken under exactly identical experimental conditions. The spectra taken at various angles were normalized so that the total edge jump (measured by the change in absorption at 275- and 310-eV photon energies) was identical. The absorption cross section for the 1s to π^* transition was measured from the height of the peak at a photon energy of 282 eV.

The Mo(100) single crystal was cut by using standard metallographic techniques and mounted on a carousel geometry manipulator. The sample could be resistively heated to 2000 K, and the temperature was measured by means of a W 5% Re/W 26% Re thermocouple spot-welded to the edge of the crystal. The sample was cleaned by using a standard procedure that consisted of heating to 1200 K in a background of 2×10^{-7} Torr of oxygen and annealing under vacuum at 2000 K. The sample was adjudged clean when no impurities (primarily oxygen and carbon) were detectable with Auger spectroscopy. In order to ensure that there was no remaining carbon contamination on the surface prior to dosing, the sample was cooled in the presence of 1×10^{-8} Torr of oxygen, and a thermal desorption experiment was performed to monitor 28 amu (CO). No carbon monoxide desorption was detected, indicating that the sample was free of carbon.

Auger experiments were carried out on a Varian four-grid RFA. The chamber was also equipped with a multichannel capillary array for sample dosing and with a shielded quadrupole mass spectrometer for leak testing and residual gas analysis. Angle-integrated photoelectron spectra were obtained by using a cylindrical mirror analyzer and ultraviolet light from an inert gas discharge source. All angle-integrated photoelectron spectra shown below were obtained by using HeI radiation (20.2 eV).

The butadiene was purified by several bulb-to-bulb distillations and stored in glass. No impurities were detected mass spectroscopically.

3. Results

An angle-integrated photoelectron spectrum of a Mo-(100) surface exposed to butadiene at 150 K was taken with HeI radiation, and the resulting spectrum is shown in Figure 1a. Shown also for comparison is the spectrum due to the clean metal (Figure 1b) to indicate which peaks are due to metal d-bands. Shown for comparison are the results from a calculation of the density of states of molybdenum,[16,17] which agree well with the experimental photoelectron spectrum. The extra peak at the Fermi level is due to a surface state.

Butadiene-induced peaks are clearly visible on the background of inelastic electrons (Figure 1a). The spectrum exhibits a sharp peak at 4.2 eV binding energy (BE), a broad peak centered at 7-eV BE, an intense peak at 8.4-eV BE, a peak at 10.3 eV, and perhaps a small peak at 12.9 eV, but since this latter peak is close to the inelastic cutoff, its existence may be doubtful. The peak positions
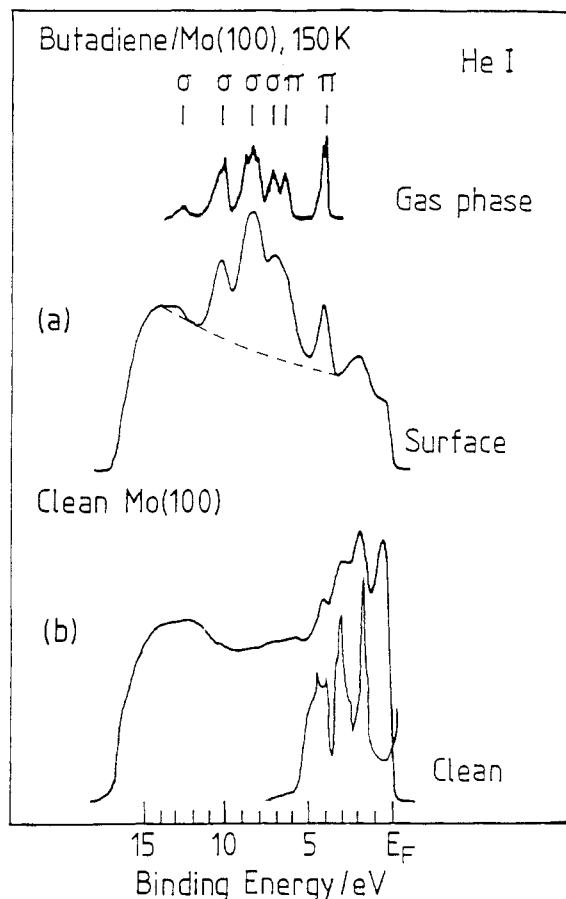
(15) Fulmer, J. P.; Zaera, F.; Tysoe, W. T. *J. Chem. Phys.* **1987**, *87*, 7265.

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Figure 1. Angle-integrated ultraviolet photoelectron spectrum of (a) butadiene adsorbed on Mo(100) at 150 K. Shown for comparision is the gas-phase spectrum of butadiene shifted so that the σ-levels coincide. Spectrum b is of a clean metal surface. Shown also for comparison is a calculated density of states for clean molybdenum.

are compared to those of a gas-phase photoelectron spectrum of butadiene in Figure 1,[18] and clearly there is good agreement between the peak positions in the two spectra, bearing in mind the slightly lower resolution of the spectrum of the surface species. The position of the inelastic cutoff in the case of a butadiene-covered surface (16.70 eV) is different than that of the clean metal (16.90 eV). This change in inelastic cutoff corresponds to a work function increase of $\sim$0.2 eV.

In order to determine the orientation of this species with respect to the surface, a series of angle-resolved spectra were taken by using 30-eV photons from a synchrotron (Figure 2). The exact shape of this spectrum differs slightly from that shown in Figure 1, partly because the spectra shown in Figure 2 are angle-resolved spectra and also partly due to the different photon energies used. Comparison with the peak positions in the gas-phase spectrum, however, yields good agreement. The spectra in Figure 2 are shown taken at different angles of incidence of the UV beam (Θ), and in all cases photoelectron emission is measured normal to the surface.

Molecular orientation can also be measured from the angular variation of the near-edge adsorption structure. Figure 3 shows the NEXAFS curves taken at the carbon edge following adsorption of butadiene onto Mo(100) at 120 K taken at normal, 25°, and 45° incidence. In this case, the absorption cross section was measured by using

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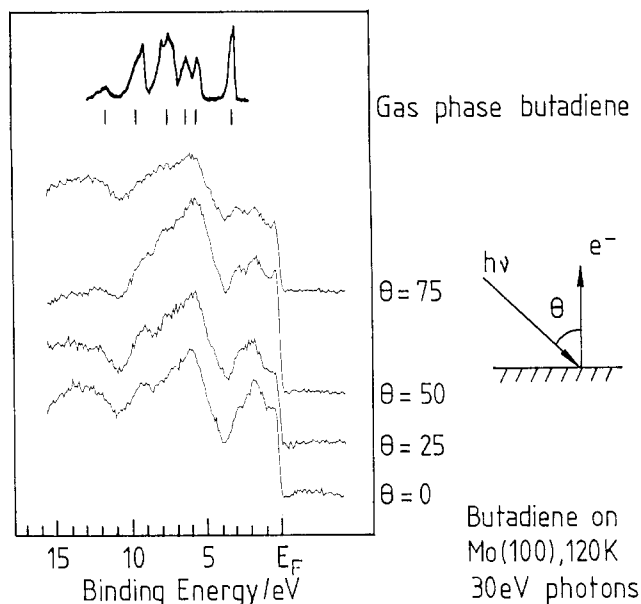
Figure 2. Series of angle-resolved ultraviolet photoelectron spectra of butadiene adsorbed on Mo(100) at 120 K taken as a function of angle of incidence for normal detection.
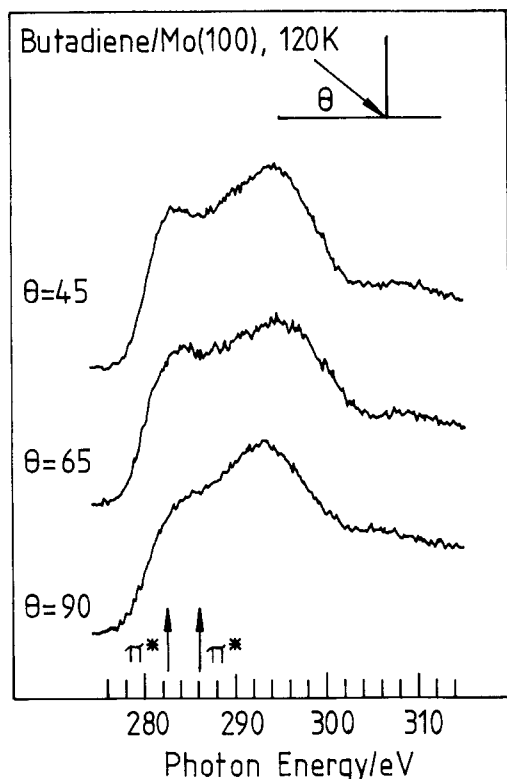

Figure 3. Series of near-edge X-ray absorption fine-structure spectra of butadiene adsorbed on Mo(100) at 120 K taken as a function of angle of incidence by using Auger detection of the absorption cross section.

the Auger electrons emitted due to the decay of the core hole. The spectra show a relatively broad peak centered at a photon energy of 284 eV, which grows as the incidence angle of the photons (measured with respect to the surface) decreases. In addition, the spectrum exhibits a broad peak centered at $\sim$296-eV photon energy.

Warming the surface slightly to 200 K yields a completely different angle-integrated photoelectron spectrum (Figure 4), indicating a low-temperature transformation of chemisorbed butadiene to a new species. In order to emphasize the adsorbate-induced peaks, an estimated
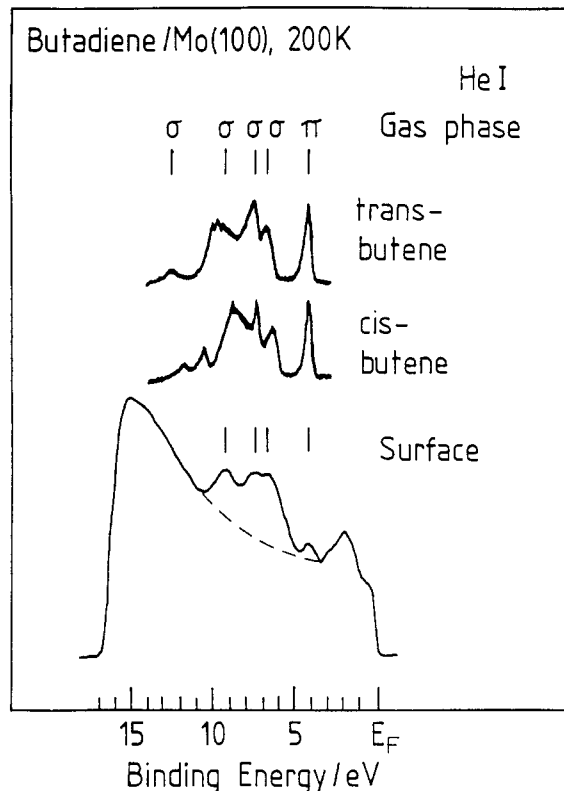

Figure 4. Angle-integrated ultraviolet photoelectron spectrum of a butadiene surface dosed at 150 K which has been warmed to 200 K. Shown for comparison are gas-phase spectra of cis- and trans-butene.

Table I. Assignment of Absorbate-Induced Peaks following Butadiene Adsorption on Mo(100) at 150 K

BE/eV	assignment
4.2	$1b_g$ (π)
7.0	$1a_u$ (π)
8.4	$6b_u$ (σ), $7a_g$ (σ)
10.3	$5b_u$ (σ), $5a_g$ (σ)
12.9	$4b_u$ (σ),

inelastic baseline is drawn in the spectrum of Figure 4. The spectrum exhibits adsorbate-induced peaks at 4.3-eV BE, a doublet with components at 6.7- and 7.7-eV BE, and a peak at 9.3 eV.

4. Discussion

The photoelectron spectrum of the d-band region of molybdenum shows good agreement with the calculated density of states (Figure 1). Since heating a Mo(100) surface to 150 K completely desorbs any condensed butadiene,[13] the spectrum shown in Figure 1 is due to photoemission from chemisorbed butadiene. The Mo(100) surface shows a work function change of +0.2 eV following butadiene adsorption, which implies electron donation from the surface to the chemisorbed butadiene molecule. A bonding mode in which electrons are donated to adsorbed butadiene is in general agreement with the calculations of Baetzold[14] where, in the case of an fcc surface with a value of N_d (number of d electrons) = 5.0, the chemisorbed molecule is calculated to have a residual charge of $\sim-1e$. The magnitude of the work function change is, however, much too small for a net $-1e$ charge on the butadiene and suggests that the calculation overestimates this value.

The excellent agreement between the gas-phase photoelectron spectrum of butadiene and the peaks following butadiene adsorption at 150 K allows the peaks to be

**Table II. Irreducible Representations of Flat-Lying
Butadiene Assuming C_2 Symmetry[a]**

BE/eV	irreducible representation and transformation properties
4.2	$b(x,y)$
7.0	$a(z)$
8.4	$b(x,y)$, $a(z)$
10.3	$b(x,y)$, $a(z)$
12.9	$b(x,y)$

[a] Z is perpendicular to the metal surface.

assigned directly, and these assignments are given in Table
I. There is some indication that the peak at 7.0-eV BE
might have a low binding energy shoulder due to the $1a_u$
(π) level. It is of interest to note that the π levels, par-
ticularly that at 4.2 eV ($1b_g$, π), are not shifted relative to
the peaks of the σ-framework of the molecule. This ob-
servation is also in agreement with the calculations of
Baetzold[14] in which butadiene chemisorbed on a metal
which lies near the center of the transition series (char-
acterized by N_d = 5.0) has *occupied* π orbitals that have
binding energies that are not significantly perturbed from
the gas-phase values. This is because bonding on these
surfaces is predominantly due to interaction of the metal
d-levels with the unoccupied adsorbate antibonding or-
bitals, which results in donation of electrons *from* the metal
to the adsorbate.

Baetzold calculates an equilibrium geometry for buta-
diene in which the plane of the molecule lies parallel to
the surface on an fcc (111) metal. We turn our attention,
therefore, to the measurement of the molecular orientation
of chemisorbed butadiene adsorbed at low temperature
onto Mo(100) using angle-resolved photoelectron spec-
troscopy from the data of Figure 2. Adsorbing butadiene
so that its molecular plane is no longer perpendicular to
the surface reduces the molecular symmetry to a C_2 point
group by removing a mirror plane. The irreducible rep-
resentations and transformation properties of the buta-
diene molecular orbitals assuming this point group are
shown in Table II. It is clear that the peaks of A sym-
metry (A_u and A_g in gas-phase butadiene) are suitable for
the measurement of the molecular orientation angle since
they transform as a vector perpendicular to the molecular
plane. Measurement of the variation in intensity of pho-
toemission peaks from orbitals of this symmetry yields the
orientation of the z-axis (i.e., the principal axis) of the
molecule with respect to the surface normal. A set of
theoretical calculations of the variation of intensity of
photoemission from a peak of A symmetry as a function
of incidence angle for various angles of the molecular z-axis
to the surface normal is shown in Figure 5. The calcu-
lations are performed for 30-eV photons, since they take
account of the optical properties of the surface at this
energy.[15] Plotted also on this figure are experimental
points taken from the spectra of Figure 5 by using the
7.0-eV BE peak, which transforms exclusively as z. Note
that the 8.4-, 10.3-, and 12.9-eV BE peaks are not suitable
for this measurement since they are of mixed symmetry,
and the π peak at 4-eV binding energy is partly obscured
by the substrate d-electrons. Peak heights were measured
by drawing in an estimated baseline due to inelastic
electrons. The error bars in Figure 5 are drawn to take
account of possible variations in the baseline. Comparison
of the experimental data with the theoretical curves
(Figure 5) suggests that the molecular z-axis is tilted at
40° ± 5° to the surface normal. That is, since the principal
C_2 axis is perpendicular to the molecular plane in buta-
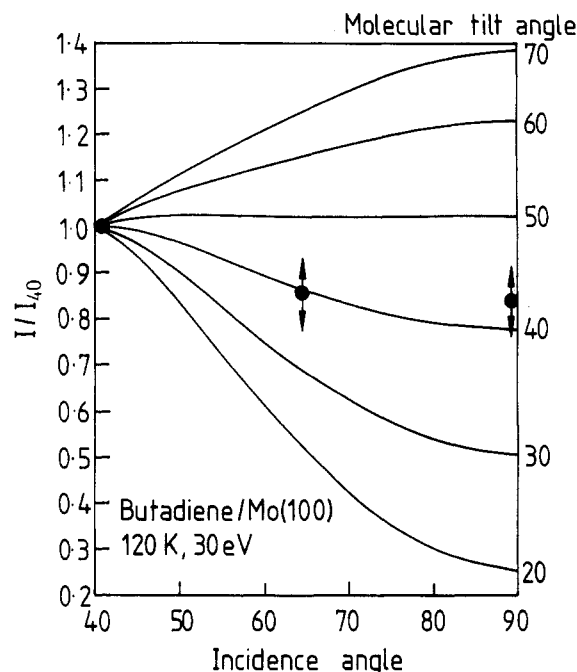diene, the molecular plane is tilted at ~40° to the Mo(100)

Figure 5. Plot of the ratio of photoemission intensity normalized
to emission at 40° as a function of incidence angle. Shown plotted
for comparison are a set of theoretical plots for various molecular
tilt angles.

surface. This result is at variance with theoretical calcu-
lations. However, the experimental data are for a (100)
bcc surface, whereas the equilibrium geometry is calculated
for a (111) fcc surface.

We turn our attention now to the NEXAFS data of
Figure 3. The spectra show a reasonably sharp peak
centered at ~282 eV, which is assigned to absorption into
the π^* orbitals of butadiene. Butadiene has two unoccu-
pied π levels: π_3^* of A_u symmetry and a π_4^* level of B_g
symmetry in the gas phase. The calculated positions of
these orbitals in gas-phase butadiene are marked on the
spectra in Figure 3. The broad peak centered at 284-eV
photon energy is assigned to σ^* resonances. According to
Baetzold, the π_3 level interacts strongly with the metallic
levels and is significantly broadened and shifted, and this
may account for the width of the NEXAFS structure in
this region. Nevertheless, both antibonding π levels are
antisymmetric with respect to the molecular plane and
therefore have identical angular dependences, the cross
section being proportional to

$$(3 \cos^2 \alpha - 1)(3 \cos^2 \Theta - 1) + 2$$

where α is the angle between the electric field and the
surface normal and Θ is the angle between the molecular
plane and the surface. Analysis of the data shown in
Figure 3 (for Θ = 90°, 65°, and 45°) indicates that the
molecular plane is tilted at 45° ± 10° to the surface plane.
This is, within experimental error, in rather good agree-
ment with the data from photoelectron spectroscopy.

Warming the butadiene-covered Mo(100) surface to 200
K yields a completely different set of adsorbate-induced
peaks (Figure 4). The onset of hydrogen desorption fol-
lowing butadiene adsorption onto clean Mo(100) at low
temperature is at ~200 K.[13] This temperature is some-
what lower than the onset of hydrogen desorption following
the exposure of Mo(100) to H_2, which is at ~250 K.[19] This
suggests that butadiene chemisorbed on Mo(100) does not
dehydrogenate until *above* 200 K. Comparison of the

(19) Zaera, F.; Kollin, E. B.; Gland, J. L. *Surf. Sci.* **1986**, *166*, L149.

adsorbate-induced peak positions with those of unsaturated C_4 hydrocarbons (i.e., *cis*- and *trans*-butene), which are also shown in Figure 4,[18] suggests that the surface species that arises by warming the surface to 200 K corresponds to *trans*-2-butene. It should be emphasized that the adsorbate-induced peak positions do not yield such good correspondence to any other C_2, C_3, or C_4 hydrocarbons and that the gas-phase spectra have been rigidly shifted to obtain the agreement shown in Figure 4. Since thermal desorption spectroscopy indicates that 200 K is below the temperature at which surface species dehydrogenate, it is proposed that the change in the spectrum is due to a thermal transformation of the surface species rather than self-hydrogenation of the butadiene.

Finally, the inelastic cutoff in the spectrum in Figure 4 is at 16.8 eV, corresponding to a work function increase of ~0.1 eV compared to the clean surface. In this case, the surface work function differs only slightly from that of the clean metal, indicating a lower extent of electron transfer from the substrate to the adsorbate than in the case of molecular butadiene. The transformation of chemisorbed butadiene to the *trans*-butene-like species is thermally induced and therefore slightly activated. The observation of such a thermal transformation is in agreement with the calculations of Baetzold.[14] These suggest that there should be a considerable strengthening of the middle C–C bond with a concomitant weakening of the terminal C–C bonds of butadiene on chemisorption, especially for chemisorption on metals toward the center of the periodic table. This prediction is entirely consistent with the experimental observations since, in contrast to butadiene, in butenes the bond order of the middle carbon

is larger than for the terminal carbons.

5. Conclusions

The results of our spectroscopic investigation of the low-temperature chemisorption of butadiene on Mo(100) are substantially in agreement with the results of a tight-binding calculation by Baetzold.[14] That is, the occupied orbitals of butadiene are only slightly perturbed when it is chemisorbed on a metal toward the center of the transition series (characterized by N_d = 5.0). Bonding to the surface is by electron donation from the metal to the adsorbed molecule since chemisorption is accompanied by a work function increase.

The molecular plane is tilted at ~40° to the surface following chemisorption of butadiene on Mo(100) at 120 K. Warming a butadiene-covered surface to 200 K results in the thermal transformation of butadiene to a different species having a photoelectron spectrum that corresponds well to that of gas-phase *trans*-2-butene. This observation is in line with theoretical predictions which suggest that the middle C–C bond of butadiene should be strengthened relative to terminal C–C bonds on chemisorption.

Registry No. Mo, 7439-98-7; butadiene, 106-99-0.

Dispersion Polymerization of Styrene in Polar Solvents. Characterization of Stabilizer in Ordinary and Precipitated Particles by Fluorescence Quenching

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Fluorescence-quenching experiments were performed on methanolic and aqueous suspensions of dispersion-polymerized polystyrene (PS) particles stabilized with pyrene-labeled (hydroxypropyl)cellulose (HPC). The results were compared to those obtained from novel precipitated particles, prepared by dissolving the original dispersion-polymerized particles in dioxane and precipitating with controlled addition of methanol. For particles dispersed in methanol, Stern–Volmer plots of I_0/I vs [quencher] were nonlinear for quenchers ethylpyridinium bromide (EPB) and *N,N*-dimethylaniline (DMA), saturating at a value of I_0/I consistent with an inaccessible fraction of fluorophores. With a modified Stern–Volmer model, the accessible fraction was calculated to be 0.5 for EPB quenching and 0.65–0.75 for DMA quenching. Remarkably similar results were obtained from the original and precipitated particles. These results support a morphological model with most of the steric stabilizer (i.e., the accessible fraction of fluorophores) located in a thin layer of grafted HPC–PS on the particle surface in both kinds of particles. For particles dispersed in water, quenching by DMA was shown to involve significant swelling of the particles by DMA, with solution-based quenching being dominant.

Introduction

During dispersion polymerization, an initially homogeneous reaction mixture containing monomer, initiator, solvent, and steric stabilizer reacts to form polymer particles 0.1–15 μm in diameter, often of excellent monodispersity. The dispersion polymerization of styrene in polar solvents has been the object of a detailed mechanistic investigation in this laboratory.[1,2] One aspect of this work

addressed issues concerning the role of the stabilizer in dispersion polymerization.[2] Focussing on one steric stabilizer, (hydroxypropyl)cellulose (HPC), demonstrated that

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