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THE SURFACE STRUCTURE OF COADSORBED BENZENE AND CARBON MONOXIDE ON THE RHODIUM (111) SINGLE CRYSTAL DETERMINED FROM LOW-ENERGY ELECTRON DIFFRACTION INTENSITIES

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Abstract

The first structural determination of a molecular coadsorbate system is presented. Mutual reordering and site shifting are found to occur for benzene and CO coadsorbed in a \( (31) \) lattice on Rh(111). This Low-Energy Electron Diffraction (LEED) intensity analysis yields the first confirmed hollow-site adsorption of CO on a single-crystal metal surface, with a C-O bond length expanded by 0.06 ± 0.05 Å from the gas phase. The flat-lying benzene is centered over hcp-type hollow sites with a strong Kekulé-type distortion: C-C bond lengths alternate between 1.33±0.15 and 1.81±0.15 Å (hydrogen positions were not determined). This suggests the possibility of a 1,3,5-cyclohexatriene species being formed. The Rh-C bond length is 2.35±0.05 Å for benzene and 2.16±0.04 Å for CO.

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1. Introduction

A growing amount of structural information is becoming available on monolayers of aromatic molecules adsorbed on transition metal surfaces.\textsuperscript{1} The main techniques used to obtain such information are High-Resolution Electron Energy Loss Spectroscopy (HREELS), Low-Energy Electron Diffraction (LEED), Thermal Desorption Spectroscopy (TDS), Angle-Resolved Ultraviolet Photoemission Spectroscopy (ARUPS), and Near-Edge X-Ray Absorption Fine Structure (NEXAFS). We report here on the structure of benzene adsorbed on the Rh(111) single-crystal surface in the presence of coadsorbed carbon monoxide. LEED intensity analysis and HREELS were the primary techniques used in this study. This is the first structure analysis of a two-molecule adsorption system to yield detailed information on the bonding of both molecules to the metal. The interaction between these coadsorbates shows up both in ordering and in bonding effects: the long-range order depends on the relative coverage (concentration) of the two molecules, and each molecule bonds very differently to the metal than in the absence of the other molecule.

Our structural results also aid the understanding of chemical reactions involving aromatic molecules on metals. Examples of such reactions include the cyclization of acetylenes to arenes as catalyzed by organometallics,\textsuperscript{2} or as catalyzed by metal surfaces, especially Pd(111),\textsuperscript{3} and the newly observed reaction of benzene conversion to acetylene.\textsuperscript{4}
We previously reported\textsuperscript{5} the benzene adsorption geometry for the same system discussed here, Rh(111)-c(2\sqrt{3}x4)\text{rect} or \text{-(\textsuperscript{3}1\textsubscript{13})}, also obtained by a LEED intensity analysis (the c(2\sqrt{3}x4)\text{rect} notation is totally equivalent to the (\textsuperscript{3}1\textsubscript{13}) matrix notation\textsuperscript{6}). However, it was not recognized at the time that CO was coadsorbed in an ordered manner with the benzene and therefore no CO was included in the LEED calculations (the presence of CO was known,\textsuperscript{7} but assumed unimportant to the benzene ordering). The ordering role of coadsorbed CO for organic monolayers on metal surfaces was established by more recent HREELS and TDS experiments performed in this research group.\textsuperscript{8} This finding required a re-analysis of the LEED data, including coadsorbed CO in the calculations. It is found that the optimum benzene structure does not change qualitatively when coadsorbed CO is included in the calculations. Thus, our initial benzene structure\textsuperscript{5} is substantially confirmed in this work.

2. Structure Analysis

2.1 LEED data

The Rh(111) surface was prepared by standard techniques,\textsuperscript{7} while LEED intensities were obtained by the photographic method.\textsuperscript{7} In our LEED intensity analysis, we have used intensity-energy (I-V) curves for 13 symmetry-inequivalent beams measured at normal incidence of the incoming electrons. These beams are labeled (0,-1), (0,1), (\textsuperscript{1}{4},\textsuperscript{1}{4}), (0,\textsuperscript{1}{4}), (\textsuperscript{1}{4},0), (\textsuperscript{1}{4},\textsuperscript{1}{4}), (\textsuperscript{1}{4},\textsuperscript{1}{4}), (\textsuperscript{1}{4},0), (0,\textsuperscript{1}{4}), (\textsuperscript{1}{4},\textsuperscript{1}{4}), (\textsuperscript{1}{4},0), (\textsuperscript{1}{4},0). Photographs and labeling of the (\textsuperscript{3}1\textsubscript{13}) pattern are shown in Reference 7. The energy range used for comparison
with theory was \( 20 \leq E \leq 150 \) eV, yielding a cumulative non-degenerate energy range of 1224 eV. These are the same experimental data described previously.\(^5\)

2.2 **LEED theory**

In the LEED intensity calculations, we have applied the new approximation method called Beam Set Neglect, described and tested before.\(^5\)\(^9\) It allows overlayer unit cells of any size and shape to be treated very efficiently by drastically reducing the number of diffraction beams calculated simultaneously. Intralayer multiple scattering within the adsorbate layer was approximated as follows in the new set of calculations (hydrogen is ignored as before). While all internal multiple scattering was included within individual molecules (by use of Reverse Scattering Perturbation and Matrix Inversion\(^10\)), we ignored all intralayer multiple scattering between molecules. The latter method is particularly efficient, since it can be cast in the form of a simple kinematic summation of the beam scattering properties of the benzene overlayer and of the carbon monoxide overlayer taken separately (we call this "Kinematic Sublayer Addition" or KSLA). A benefit of this approach is that many different relative positions of the inequivalent molecules can also be obtained efficiently: the only computational step that must be repeated is the economical stacking of layers by Renormalized Forward Scattering.\(^10\) In the present case, the combination of BSN and KSLA led to computing costs of only about \$3\ per structure. This constitutes a reduction by one to two orders of magnitude compared to conventional theoretical techniques.\(^10\) The
approximations used here yield this computational advantage at little
cost in accuracy, especially when kinetic energies $E$ well above 10 eV
are used. For the purpose of structural determination, these
approximations give rise to uncertainties that are no larger than the
uncertainties inherent in the more accurate conventional methods due to
the muffin-tin model of the atomic potential, the homogeneous damping
model and the use of Debye-Waller factors.\textsuperscript{11}

While the KSLA scheme has been tested successfully before in
several cases\textsuperscript{5,11-12} we still need to justify its use in the present
situation. KSLA's requirement of negligible intermolecular multiple
scattering is certainly well satisfied by hydrocarbon molecules that
are kept separated at Van der Waals distances between their respective
hydrogen atoms, since the hydrogens do not scatter appreciably: this
has been verified previously without BSN\textsuperscript{11} and in the course of this
work with BSN. When hydrogen atoms are not available as "cushions"
between molecules to keep the carbon atoms far apart, a small amount of
intermolecular multiple scattering can occur. We have previously
observed\textsuperscript{12} this to induce errors in the structural determination of
less than 0.1 Å (in the case of a layer of close-packed adsorbed CO
molecules). The hydrogen "cushions" of our present structure,
therefore, should ensure a good accuracy.

We have applied R-factors to evaluate the level of agreement
between theoretical intensities $I_t$ and experimental intensities $I_e$ for
the various structural models. We have used the following five
R-factors together with their average, as in our initial study of this
structure\textsuperscript{5} and of many other molecular adsorbate structures.\textsuperscript{11-13}

\( \text{ROS} = \frac{\text{fraction of energy range with slopes of opposite signs in the experimental and theoretical I-V curves,}}{0.75 \int |I_e - cI_t|dE \int |I_e|dE,} \\
\( R1 = 0.5 \int (I_e - cI_t)^2 dE \int I_e^2 dE,} \\
\( RRZJ = 0.5 \int \{ \frac{|I_e'' - cI_t''| \|I_e' - cI_t'|}{\|I_e'\| + \max |I_e'|} \} dE / (0.027 \int |I_e|dE),} \\
\( RPE = 0.5 \int (Y_e - Y_t)^2 dE / \int (Y_e^2 + Y_t^2) dE, Y(E) = L / (1 + V_{01}^2 L^2), L = I'/I.} \\
\)

Here \( c = \int |I_e|dE / \int |I_t|dE \) and the apostrophe denotes differentiation with respect to the energy. \( RRZJ \) is the reduced Zanazzi-Jona R-factor, while \( RPE \) is Pendry's R-factor, both renormalized with a factor 0.5 to match the scale of the other R-factors (\( V_{01} \) is an estimate of the imaginary part of the inner potential, here 4 eV). We shall mainly use the average over these five R-factors, but we shall also quote \( 2 \times RRZJ \) and \( 2 \times RPE \) to allow comparison with other work.

2.3 Adsorption structures tested

The number of potentially correct structures for \( C_6H_6 \) and CO coadsorbed on Rh(111), even within a given two-dimensional unit cell, is enormous. Since in a LEED intensity analysis all potentially correct structures must be tested, we rely on additional information obtained by non-LEED techniques to narrow down the possibilities. Recent Thermal Desorption Spectroscopy experiments\textsuperscript{6} imply that: 1. The
majority of the adsorbed benzene molecules are intact at the temperature of the LEED experiment; 2. In the \((\{^{\text{31}}_{13}\})\) structure there is an equal number of benzene and CO molecules, corresponding to about 1/8 of a monolayer of each (here 1 monolayer corresponds to one adsorbate molecule for each surface metal atom; in these units, benzene saturates the surface at about 1/6 monolayer and CO saturates the surface at about \(\%\) monolayer). Further High-Resolution Electron Energy Loss Spectroscopy experiments\(^8\) imply that: 1. The benzene molecules are not only confirmed to be intact, but they lie parallel to the surface, rather than being bonded to the metal through their periphery; 2. The presence of CO is responsible for the \((\{^{\text{31}}_{13}\})\) unit cell, implying its presence within the unit cell, rather than in a disordered manner; 3. The C-O stretch frequency is such that the CO molecules are most likely bonded with threefold coordination to the metal surface, i.e. in hollow sites.

These results indicate that each \((\{^{\text{31}}_{13}\})\) unit cell contains one CO molecule (\(~1/8\) monolayer) in addition to a single flat-lying benzene molecule. The vacancy left between benzene molecules has the right size to accommodate this single CO molecule, but only if one assumes the particular benzene orientation about its axis shown in Figure 1. Because of steric hindrance between CO and benzene, the two molecules must be centered on the same kind of adsorption site, e.g. hcp-type hollow sites for both molecules, as illustrated in Figure 1.

We have made LEED intensity calculations for a single upright-standing CO molecule and a single flat-lying benzene molecule (with the
orientation of Figure 1) in each unit cell for four different registries, i.e. four different high-symmetry adsorption sites: top, bridge, and both kinds of hollow sites (hcp hollow and fcc hollow). In the CO molecules, the CO bond axis was fixed perpendicularly to the surface and the C-O bond length was varied between 1.15Å and 1.25 Å (the C-O bond length varies by less than 0.1 Å from one adsorption site to another in metal-carbonyl clusters$^{14}$ and on surfaces$^{12}$). The heights of the two molecules above the metal substrate were varied independently of each other. The metal substrate was kept bulk-like: significant substrate distortions are unlikely, based on results for other molecular adsorbates on Rh(111)$^{12-13}$.

In a first stage of the structural determination the carbon ring was given its gas-phase geometry (hexagonal symmetry with equal C-C bond lengths of 1.397Å) and the C-O bond had its gas-phase value of 1.15Å. This allows the adsorption sites and molecular heights to be approximately determined. Then, in the favored hcp-hollow site, the benzene ring was given a wide range of Kekulé distortions, i.e. alternating long and short C-C bonds. Simultaneously, the heights of the two molecules over the metal surface were still varied, but with a constant mutual height difference. Without CO, out-of-plane bucklings of the carbon ring have been tested and found to be very unlikely, while a large Kekulé distortion was already observed.$^5$

Kekulé distortions involve atomic motions parallel to the surface. We found our LEED analysis to be relatively sensitive to such displacements. We tentatively ascribe this to our large data base,
which includes many beams emerging at far off-normal angles. Because many LEED analyses do not share this feature, and because of the potential importance of such distortions, further tests of the optimal Kekulé-type structure were performed: the analysis was repeated with different relative heights of the benzene and CO, with different values of the topmost Rh-Rh interlayer spacing, with the number of phase shifts increased from 5 to 6, with matrix inversion as opposed to a perturbation expansion for the multiple scattering within the molecules, with different values of the muffin-tin zero level (varied at the R-factor stage), with individual as opposed to averaged R-factors and with R-factor comparisons involving subsets of the available beams. Under all these modifications, the optimal atomic positions changed by less than 0.1Å, both perpendicular and parallel to the surface. Finally, with a fixed benzene distortion, the C-O bond length was varied, as well as the mutual height difference between the two molecules. This resulted in minor corrections and therefore the structural search was stopped at that stage. In all, about 440 different coadsorption geometries were examined by LEED in this work, in addition to about 960 structures reported\(^5\) in our initial work without CO.

3. Results

Our best structure for Rh(111)-\((^{31}_{13})\)C\(_6\)H\(_6\)+CO, i.e. the structure which minimizes the R-factors, is illustrated in Figure 1 (the H positions are guessed). Both benzene and CO occupy hcp-type hollow sites in a compact arrangement. The benzene carbon ring has a spacing
of 2.25±0.05Å to the metal surface with six identical Rh-C bond lengths of 2.35±0.05Å. The substantial Kekulé-type distortion is evidenced in the R-factor contour plot shown in Figure 2: C-C bond lengths alternate between 1.33±0.15Å and 1.81±0.15Å, the short bonds lying over the top of single metal atoms. Such a structure respects the local binding-site symmetry, which is $C_{sV} \sigma_d$. This benzene structure is very similar to our previously published structure for this system, obtained by ignoring the CO coadsorption.

The optimal metal-carbon interplanar spacing for CO in our structure is 1.50±0.05Å, corresponding to a Rh-C bond length of 2.16±0.04Å. The best C-O bond length is found to be 1.21±0.05Å.

The optimal structure has values of the Zanazzi-Jona R-factor, Pendry R-factor and five-R-factor average of 0.40, 0.66 and 0.31, respectively (these values can vary by ±0.10, ±0.10 and ±0.03, respectively, as the theoretical method is changed). The best muffin-tin zero level, a non-structural parameter which is optimized at the same time as all the structural parameters, is 8±1 eV below vacuum.

4. Discussion

4.1 Coadsorption-Induced Ordering

A remarkable occurrence in the coadsorption of benzene and CO on Rh(111) is the mutual reordering of the two species, i.e. the change of each other's long-range periodicity. It is known that neither pure
benzene overlayers nor pure CO overlayers produce a \((\frac{31}{13})=c(2\sqrt{3}x4)\text{rect}\) periodicity on Rh(111). Indeed, benzene without CO orders, at saturation coverage, in a \((2\sqrt{3}x3)\text{rect}\) structure; and CO without benzene orders in \((\sqrt{3}x\sqrt{3})R30^\circ_{13}\) or \((2x2)_{12}\) structures, depending on the coverage. Furthermore, increasing the CO coverage to \(~2/9\) monolayer in the presence of \(~1/9\) monolayer of benzene yields a \((3x3)\) coadsorption structure\(^7,8\) (compared with \(1/8\) monolayer of CO and \(1/8\) monolayer of benzene in the \((\frac{31}{13})\) structure).

This example of ordering modified by coadsorption illustrates a general phenomenon: coadsorption can be used to modify long-range order. One can even create long-range order when there was none, as in the case of CO added to benzene on Pt(111)\(^8\). Similar behavior has been encountered\(^8\) for CO coadsorbed with other adsorbates, such as ethylidyne, methylacetylene, propylidyne, chloro- and fluorobenzene and sodium, on Rh(111), as well as with NO rather than CO as a coadsorbate on Rh(111)\(^15\). The added variety of structures due to coadsorption helps solve surface structures by providing more closely-related test cases. Especially helpful is the situation where a disordered overlayer is induced to order, simplifying the structural determination. Furthermore, closely-related results contribute to chemical understanding due to their mutual small chemical differences, as we shall illustrate next.

4.2 Adsorption sites

It appears that the equilibrium adsorption site of both benzene and
CO is modified by their coadsorption. For CO this is firmly established: without benzene or other coadsorbates, CO adsorbs in either 1-fold coordinated top sites or (above 1/3 monolayer coverage) also in 2-fold coordinated bridge sites, but never in 3-fold coordinated hollow sites, as is known from HREELS and LEED.\textsuperscript{12-13,16a} Our finding of a hollow site for CO in the presence of benzene is the first crystallographic evidence for hollow site occupation by CO on any metal surface. The recent HREELS measurements for this system already suggested this site,\textsuperscript{8} based on the empirical relationship between CO-stretch frequency and site occupation found in metal-carbonyl clusters.\textsuperscript{16b} This relationship states that when the C-O stretch frequency falls in the (approximate) ranges 1650-1850 cm$^{-1}$, 1850-2000 cm$^{-1}$ or 2000-2150 cm$^{-1}$, the CO molecule is adsorbed respectively in a three-, two-, or one-fold coordinated site. Our result is the first confirmation of that empirical relationship for CO in hollow sites on surfaces.

Hollow site occupation by CO on several metal surfaces, including Rh(111), has also been suggested when CO is coadsorbed with potassium or other alkali metals.\textsuperscript{17} There, a mechanism of charge transfer from potassium to CO via the metal substrate has been proposed. By analogy, with benzene substituted for potassium, a similar mechanism can be proposed involving charge donation by the benzene $\pi$-ring orbitals. This would be consistent with the known electron-donating character of benzene, as detected by work function measurements.\textsuperscript{18}
The effect of CO on the benzene adsorption site is less well established because no LEED intensity analysis of the CO-free benzene structure has been performed. However, the observed \((2\sqrt{3}\times3)\) rect structure of pure benzene on Rh(111) appears to possess glide-plane symmetry, which can best be explained by bridge-site adsorption (a full LEED intensity analysis of this structure is in preparation). If a site change from bridge to hollow is indeed induced by CO, presumably the same charge transfer mechanism from benzene to CO mentioned above could be held responsible: the presence of CO would withdraw more charge from benzene, causing a site change. However, the assignment of a benzene adsorption site based on HREEL spectra is not fully resolved at this stage, despite extensive work.\(^1f,18,19\)

4.3 CO bond lengths

The Rh-C bond length for CO is found to be \(2.16\pm0.04\) Å in the hollow site. This is compared in Table 1 with values for bridge and top sites on rhodium surfaces and in small rhodium-carbonyl clusters. A good correspondence is observed, which gives additional confidence in the overall structure determination. Note the clear site dependence of the metal-C bond length: it increases markedly on moving from 1- to 2- to 3-fold coordination. This is true both in metal carbonyl clusters and for CO adsorbed at metal surfaces.

The C-O bond length is found to be \(1.21\pm0.05\) Å, which is expanded by \(0.06\pm0.05\) Å with respect to the gas-phase value. This result may be
compared with a similar expansion of the C-O bond by 0.12±0.03 Å for CO coadsorption with Na on Pt(111), as detected by NEXAFS\textsuperscript{17f} (where the CO adsorption site is also likely to be a three-fold hollow site and the molecular axis is near to the surface normal). A C-O bond lengthening is in line with the observed bond weakening, as measured by HREELS,\textsuperscript{8} which takes place also with coadsorbed alkali metals.\textsuperscript{17} Specifically, the C-O stretch frequency measured by HREELS for CO/Na/Pt(111)\textsuperscript{17f} is 1690 cm\textsuperscript{-1}, while for our structure of CO/CeH\textsubscript{6}/Rh(111)\textsuperscript{8} it is 1655 cm\textsuperscript{-1}, compared with 2143 cm\textsuperscript{-1} in the gas phase.

4.4 The Structure of Benzene Adsorbed on the Rh(111) Surface

We find a strong distortion of the benzene ring, with alternating long and short C-C bonds that match the symmetry of the 3-fold adsorption site: the resulting specie may be called 1,3,5-cyclohexatriene. The carbon-ring radius is also considerably increased with respect to gas-phase benzene (1.58±0.15Å vs. 1.397Å). Our estimated error bars of ~0.15Å (based on R-factor contour plots like that of Figure 2) and our various tests described above are such that we have confidence in the presence of a distortion of this order of magnitude.

A number of organometallic clusters exist with which we may compare our result: these involve various aromatics or other cyclic molecules, including benzene,\textsuperscript{20} tri- and hexamethylbenzene,\textsuperscript{21} cyclopentadiene\textsuperscript{22} and azulene.\textsuperscript{23} These molecular species normally bond through their \textit{\pi}-orbitals to the metal atoms, i.e. such that the metal atoms lie
against the flat side of the molecules, usually centered close to the ring axis (alternatively, metal atoms may substitute for peripheral H atoms). None of these clusters, however, closely simulates a surface hollow site: none contains benzene bonded to a triplet of metal atoms.

Our Rh-C bond length of 2.35±0.05Å is in good agreement with metal-C bond lengths in those clusters, which range from 2.08 to 2.45Å. This wide range is due mostly to inequivalent positioning of different carbons of the same ring with respect to the cluster metal atoms. To a lesser extent, variations are also due to differences in metallic radii.

Most organometallic clusters show rather small deviations from the C-C distance of 1.397 Å in gas-phase benzene. The largest C6-ring distortion in a cluster which we have found in the literature concerns bis(hexamethylbenzene)ruthenium(0),21a with sequential C-C distances of 1.327, 1.498, 1.480, 1.408, 1.415 and 1.487Å (this particular ring does not have 3-fold symmetry; in fact it is strongly bent towards the "boat" shape of cyclohexane). The clearest Kekulé distortion which we have found in the literature occurs for hexamethylbenzene-tricarbonylmolybdenum,21b with sequential C-C distances of 1.399, 1.431, 1.408, 1.444, 1.407 and 1.448Å, i.e. ~0.04Å variation compared with our ~0.48Å. These examples also exhibit the general trend of a ring expansion, but not as large as ours, which increases the carbon-ring radius from 1.397Å to ~1.58Å.

Long C-C bonds are not uncommon in organic molecules in the gas
phase. Many examples of C-C bond lengths in excess of 1.60Å are found in the literature\textsuperscript{24,25} (the conventional C-C single bond length is 1.54Å). The largest values which we know of\textsuperscript{25} are 1.780 to 1.851Å in the molecules 11,11-dimethyltricyclo[4,4,1,0'1,6]undeca-2,4,7,9-tetraene and 11-methyltricyclo[4,4,1,0'1,6]undeca-2,4,7,9-tetraene-11-carbonitrile. A long C-C bond is usually explained as resulting from a conformational strain that pulls the two carbon atoms apart. This situation may apply in our surface system as well, if we assume that the closely-bonded C-C pairs of a benzene molecule attempt to move apart. The driving force could be provided by repulsive H-H interactions or more favorable adsorption sites for these acetylenic species.

Note that substantial out-of-plane distortions are common for aromatics in small organometallic clusters, because the aromatics attempt to wrap themselves around the metal cores or bind off-center. By contrast, in our case on Rh(111) there is no reason for an out-of-plane distortion of the carbon ring, given the binding site symmetry (the benzene hydrogens however are likely to bend out of plane due to the rehybridization around the carbons, as we shall discuss below). A substantial out-of-plane distortion would in any case be readily detected by HREELS. This has been illustrated by the observation with HREELS of tilts away from parallelism with the surface for C6HsCl,\textsuperscript{26} C6HsF,\textsuperscript{26} C6HsN\textsuperscript{26} and C6Hs,\textsuperscript{10} and no tilts for C6Hs\textsuperscript{1f,8,19} and C6Hs\textsuperscript{1e} on various metal surfaces.

Recently, the adsorption of benzene on metal surfaces has been
modeled theoretically.\textsuperscript{27,28,29} The complexity of the computational problem led to the use of versions of the Extended Huckel Theory. These calculations did not include coadsorbed CO. The substrates were Rh(111)\textsuperscript{27,29} and Ni, Ag and Pt(111),\textsuperscript{28} modeled as clusters of 3 to 17 metal atoms\textsuperscript{27,28,29} or as periodic surfaces in the tight-binding model.\textsuperscript{29} The preferred adsorption site appears to be a three-fold hollow site on each metal, but the bridge site is energetically close. It is thus quite plausible that CO coadsorption could induce a site change of benzene, as we seem to observe on Rh(111) upon addition of CO. In the hollow site, the same benzene orientation about its axis was found as with LEED: half the C-C bonds lie above individual rhodium atoms; this corresponds to \textit{C}_3\nu(\sigma_d) symmetry (cf. Fig. 1). The calculations also seem to give a slight preference for the hcp- hollow site over the fcc-hollow site.\textsuperscript{28}

The theoretical metal-carbon bond lengths are in reasonable agreement with the LEED results: 2.15\AA{} by Extended Hückel Theory versus \sim2.35\AA{} from LEED, on Rh(111). Regarding the benzene geometry, the major adsorption effect predicted by the theory is a C-H bond bending away from the surface plane by about 20° on Rh(111).\textsuperscript{29} This cannot be directly tested by LEED, but it would at least be compatible with the carbon positions found by LEED. It also matches well the observation that the out-of-plane C-H bending vibration is the mode which changes its HREELS frequency most upon adsorption.\textsuperscript{1f} Theory also predicts a substantial ring expansion\textsuperscript{29} by about 0.12\AA{}, compared with the LEED result of about 0.18\AA{}. The largest theoretical Kekule-type distortion yielded\textsuperscript{29} alternating C-C bond lengths of 1.50 and 1.64\AA{}.
Whatever the numerical values, a clear tendency towards C-C bond length expansion is found. This is consistent with the LEED result and with previous observations of reductions in the C-C bond order for other adsorbed unsaturated hydrocarbons, such as acetylene (C2H2)\textsuperscript{30-32} and ethylene (C2H4).\textsuperscript{31,33} For instance, with NEXAFS,\textsuperscript{31} bond lengthening to 1.45±0.03Å and 1.49±0.03Å, respectively, is observed for acetylene and ethylene on Pt(111), compared to gas-phase values of 1.20Å and 1.33Å. One would expect such a tendency due to the formation of metal-carbon bonds upon adsorption and the resulting rehybridization around the carbon atoms. Associated with the C-C bond-order reduction in benzene is a C-C bond weakening, which is evidenced by a frequency reduction in HREELS.\textsuperscript{1f} Note that the theory finds no evidence for C-H bond weakening, so that C-C bond scission is the easier decomposition pathway. The distortion seen in LEED suggests in a different way the same conclusion.

4.5 Benzene and acetylene interconversion

The observed strong distortion of benzene on Rh(111) corresponds more to a 1,3,5-cyclohexatriene specie than to benzene. Although the benzene appears to have nearly decomposed into three adsorbed acetylenic species, we have several experimental pieces of evidence to confirm that the molecules have not fully transformed to acetylene. These include the observation by HREELS of ring-vibration modes, and the observation by TDS that the benzene molecules are still intact at temperatures up to ~480K,\textsuperscript{8} well above the decomposition temperature of acetylene (~270K).\textsuperscript{34} It is, however, significant that benzene is much more likely to decompose than to desorb as the temperature is raised
(only about 2\% desorb intact)\textsuperscript{8}: this indicates that the tightly-bound benzene will more likely distort and break its $\pi$-ring stabilization than remain intact. Also, coadsorption of potassium, a net electron donor, decreases the likelihood of decomposition, at least on Pt(111).\textsuperscript{25} Therefore, we may tentatively propose that coadsorption of CO, a net electron acceptor, would enhance the decomposition of benzene by favoring distortion. Furthermore, a detailed analysis\textsuperscript{36} of the benzene decomposition products upon heating on Rh(111) (namely $-\text{CH}$ and $-\text{CCH}$ species) favors acetylene as an intermediate product, even if short-lived.

Rh, unlike Pd, does not catalyze the conversion of acetylene to benzene. Whereas such a reaction has been observed on Pd(111),\textsuperscript{3} it was not seen on the Rh(111) single-crystal surface. It is however most encouraging that the benzene-to-acetylene conversion appears to have been observed recently for the first time:\textsuperscript{4} indeed, Raman spectroscopy detected acetylene formation after benzene adsorption on supported Rh particles in the presence of coadsorbed CO in an ultra-high vacuum cell.

Hopefully, structural results such as ours for benzene on Rh(111) and others in preparation on Pt(111) and Pd(111) will help clarify the mechanisms of this reaction.

5. Conclusions

We have made the first structural determination of a molecular
coadsorbate system. It is characterized by mutual ordering and site-shifting of the coadsorbate species, benzene and CO. We have found the first confirmed hollow-site adsorption of CO on a single-crystal surface, with bond lengths that are quite consistent with comparable bond lengths in metal-carbonyl clusters.

The benzene is also hcp-hollow-sited and its carbon ring exhibits a strong Kekulé-type distortion and an expansion. This result may be connected with the mechanisms of acetylene-benzene interconversion reactions on metal catalysts.

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References


4. W.L. Parker, R.M. Hexter and A.R. Siedle, to be published.


6. The general notation (m\times3n)_{\text{rect}} indicates a rectangular unit cell with sides m\times3 and n times as long as the (1\times1) unit cell sides; the prefix "c" means "centered".

8. C.M. Mate and G.A. Somorjai, to be published.


15. G. Blackman, C.M. Mate and G.A. Somorjai, to be published.


26. C.M. Mate and G.A. Somorjai, to be published.


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References:  
a. this work;  
b. Ref. 12;  
c. Ref. 13;  
d. Ref. 14
Figure Captions

Figure 1: Structure of Rh(111)-(311)-C₆H₆+CO in side view and top view, including Van der Waals contours with radii 1.8Å for C in benzene, 1.6Å for C and O in CO and 1.2Å for H (the H positions are assumed, including possible CH bending away from the surface). The CO molecules are shown hatched. A (311) = c(2√3x4)rect unit cell is outlined. Dots between surface metal atoms denote second-layer metal atoms.

Figure 2: Contour plot (left) of the five-R-factor average as a function of C₆-ring distortion in Rh(111)-(311)-C₆H₆+CO. The distortion is parametrized by the ring radius r and the angular deviation β relative to a hexagon. These parameters are defined at right, together with the C-C bond lengths d₁ and d₂, whose corresponding values are given at left as contour lines. Other structural parameters are for the optimal geometry given in the text and shown in Figure 1 (except C-O bond length = 1.15Å and metal-C spacing = 1.45Å for CO molecules).
Fig. 1
Rh(111) \cdot c(2\sqrt{3} \times 4) \text{rect} - \text{C}_6\text{H}_6 + \text{CO}

R-factor contours for C\text{\textsubscript{6}} distortion

C\text{\textsubscript{6}} Distortion Parameters

Fig. 2
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