species that can insert CO and form oxygenate. Such a pathway might be

$$\text{C}_2\text{H}_4 + \text{CH}_3 \rightarrow \text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

A number of important and unanswered questions are pointed out from this work. We know nothing about the relative reactivity of various CH₄ species with CO, olefin, or alkyl groups on a given surface. For kinetic analysis we have assumed CH₄ reactions with CH₃ or CO as the dominant pathway to precursors of two-carbon products. Although this proposal may be reasonable, there are no separate data to support it.

**Summary**

We have constructed a model of oxygenate and hydrocarbon formation that describes well the observed kinetics from CO/H₂ reaction measured on a model Ru catalyst. Deviations of C₂ hydrocarbon and C₃ oxygenates from the Schulz-Flory relation are explained in terms of ethylene formation and reincorporation into larger hydrocarbon fragments. The role of K promoter in increasing oxygenate selectivity and decreasing rates of product formation is explained in terms of a lower surface H concentration.

Some general effects of reactant variables have been investigated to show how these affect product formation. We believe this formulation is general and can be applied to a variety of catalyst formulations.

**Acknowledgment.** We are grateful to D. R. Preuss for preparation of the catalyst samples.

**Registry No.** CO, 630-08-0; Ru, 7440-18-8.

---

**Thermal Decomposition of Benzene on the Rh(111) Crystal Surface**

**B. E. Koel,**

*Cooperative Institute for Research in Environmental Sciences and Department of Chemistry, University of Colorado, Boulder, Colorado 80309*

**J. E. Crowell,** B. E. Bent, C. M. Mate, and G. A. Somorjai*

*Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, Berkeley, California 94720* (Received: October 22, 1983)

Benzene decomposition on the Rh(111) crystal surface has been studied over the temperature range of 300-800 K by high-resolution electron energy loss spectroscopy (HREELS), temperature-programmed desorption (TPD), and low-energy electron diffraction (LEED). Our results show that benzene decomposition begins at 400 K, forming a mixture of CH and C₂H species. The relative amounts of these two species vary with temperature; at 470 K, the concentration ratio of CH to C₂H is 0.4. Above 500 K, these fragments dehydrogenate and condense to form C₄H polymers. By 800 K, the adsorbed monolayer is completely dehydrogenated, forming a polymeric carbon monolayer with a vibrational spectrum similar to that of an ordered graphite monolayer. We propose that benzene decomposition on Rh(111) proceeds by decarboxylation to form three acetylenes which immediately decompose to CH and C₂H species.

**Introduction**

Surface science studies have revealed that, during catalyzed hydrocarbon conversion reactions over metal surfaces, the active catalysts are partially covered with hydrocarbon fragments with a characteristic H/C atomic ratio.

1 Catalyst deactivation occurs when this layer dehydrogenates completely to form a graphitic overlayer. Consequently, it is important to elucidate the nature of the stable hydrocarbon fragments that might be present on metal surfaces during catalytic reactions throughout the temperature range employed in catalytic reactions. Chemisorption studies of hydrocarbon molecules on rhodium single crystal surfaces are of fundamental importance to the development of a molecular level understanding of catalysis, since rhodium is a versatile catalyst for hydrocarbon reactions.

In this study we have explored the decomposition of benzene adsorbed on the Rh(111) crystal face as a function of temperature in the range of 300-800 K. The sequential hydrogen evolution that accompanies benzene decomposition was monitored by temperature-programmed desorption (TPD). The disordered carbonaceous fragments produced on the surface were studied as a function of decomposition temperature by vibrational spectroscopy using high-resolution electron energy loss spectroscopy (HREELS). We propose structural models for the benzene decomposition fragments and suggest a mechanism for benzene decomposition on Rh surfaces. In addition, we have explored the decomposition of C₂, C₃, and C₄ alkenes and alkylns on Rh(111) and have found that, above 500 K, the adsorbed decomposition products for these hydrocarbons are the same as for benzene on this surface.


---

0022-3654/86/2090-2949$01.50/0 © 1986 American Chemical Society
adsorbed hydrocarbon fragments produced from benzene decomposition on single-crystal metal surfaces.

The structure of benzene adsorbed on the hexagonal Rh(111) crystal surface below 390 K has been discussed in previous papers, and HREELS and low-energy electron diffraction (LEED) studies show that benzene adsorbs molecularly below 390 K with the molecular ring plane parallel to the metal surface and that two binding sites (twofold bridge and threefold hollow) can be populated. Near saturation benzene coverage, a variety of LEED patterns are observed depending on the concentration of coadsorbed CO. The saturation benzene coverage on Rh(111) at 300 K is 0.17 ML (ML = monolayer, defined relative to the Rh surface atom density of 1.6 x 10^{15} atoms/cm^2), corresponding to a carbon atom coverage of 1.0 ML.

In this study, we find that the adsorbed hydrocarbon fragments produced from the thermal decomposition of benzene are independent of the initial benzene LEED pattern and the initial benzene adsorption site. From either of the two initial adsorption sites on Rh(111), benzene decomposes to form a mixture of adsorbed CH and C_2H species over the temperature range 400-500 K; we propose structural models for these species. These fragments further dehydrogenate and polymerize to CH and C_2 polymers above 500 K. Since acetylene and benzene give identical decomposition products from 400 to 800 K, we propose that benzene decomposes by decyclotrimerization through acetylenic intermediates and discuss all the experimental evidence that supports this model.

Experimental Section

The experiments were performed in two different UHV chambers (previously described) containing Auger electron spectroscopy, LEED, TPD, and HREELS capabilities and with base pressures of 1 x 10^{-10} torr. TPD measurements were made using line-of-sight mass spectrometry and a linear heating rate of 15 K/s. HREELS, the total scattering angle was fixed at 120°, so that for specular reflection θ_a = θ_s = 60° from the surface normal. Off-specular measurements were made by rotation of the sample about an axis perpendicular to the scattering plane. Typical conditions for HREELS were as follows: incident energy = 4 eV, incident current = 1 x 10^{-10} A, resolution = 6 meV (48 cm^{-1}) fwhm, and angular resolution = 4° fwhm. All HREEL spectra were taken at 300 K after flashing the adsorbed overlayers to the desired temperatures.

The Rh(111) samples were cleaned under vacuum by a combination of Ar+ sputtering (0.5-1 kV, 7 μA), annealing at 1000-1400 K under vacuum, and oxygen treatments (3 x 10^{-7} torr, 950-1250 K). AES, LEED, and HREELS were used to ensure that the surface was clean and well-ordered. Benzene and acetylene exposures were nominally 10 langmuirs (corrected for enhancement by multichannel array dosers but uncorrected for ion gauge sensitivities) to achieve saturation coverages. The crystal temperature was measured by a chromel-alumel thermocouple spotwelded to the crystal.

Spectral grade benzene (99.9%, Fischer) and benzene-d_{6} (99 at. %D, Norell Chemical) were stored over calcium hydride and used without further purification. Acetylene-d_{2} was obtained from MSD (99 atom % D) in a 1-L break-seal flask.

Results

1. Temperature-Programmed Desorption and Low-Energy Electron Diffraction Studies. Figure 1 shows TPD spectra for H_{2} desorption and C_{2}H_{4} desorption (inset) following the adsorption of a saturation coverage of benzene on Rh(111) at 290 K. Figure 1A shows that the decomposition of molecular benzene produces

---

(2) Crowell, J. E.; Mate, C. M.; Bent, B. E.; Somorjai, G. A.; Koel, B. E. *Surface Sci.*, to be submitted.
terized by an intense 800-cm\(^{-1}\) loss peak due to an out-of-plane CH bending mode, \(\gamma(CH)\). The large relative intensity of this peak is a result of the surface dipole selection rule together with the benzene bonding geometry in which the molecular ring plane is parallel to the Rh(111) surface. Ring breathing modes at 1320 and 1420 cm\(^{-1}\), and an in-plane CH bending mode at 1130 cm\(^{-1}\), are observed as weak loss peaks. The 2980-cm\(^{-1}\) peak is due to CH stretching vibrations, \(\nu(CH)\), and the peaks at 345 and 550 cm\(^{-1}\) are due to vibrations of the entire molecule against the Rh(111) surface.

In our previous studies, we found that no changes occurred in the \(\nu(Rh-C)\) modes at 345 and 550 cm\(^{-1}\) or in the relative intensity or energy of the modes between 1130 and 1420 cm\(^{-1}\) as the temperature was raised from 286 to 390 K, just below the onset of benzene decomposition. Peak shifts do occur for the \(\gamma(CH)\) and \(\nu(CH)\) loss peaks of molecular benzene, which have two components each, due to the presence of two different adsorption sites: \(\gamma(CH) = 776\) and 819 cm\(^{-1}\), and \(\nu(CH) = 3008\) and 2960 cm\(^{-1}\). The intensity ratios change from \((I_{776}/I_{3008})\) and \((I_{819}/I_{2960})\) of \(-0.3\) to \(-1.6\) as the relative populations of the sites change, which causes small apparent shifts in the \(\gamma(CH)\) and \(\nu(CH)\) peaks at 50-cm\(^{-1}\) resolution.

Several spectra obtained after heating the benzene monolayer to temperatures in the range 390–470 K showed that benzene decomposition begins near 410 K. In the vibrational spectrum taken after heating to 410 K (not shown here), the 800-cm\(^{-1}\) loss peak is broadened by 30 cm\(^{-1}\) (to 113-cm\(^{-1}\) fwhm) compared to that observed at 390 K, and there is also enhanced intensity at 1365 cm\(^{-1}\). However, these peaks still contain significant features due to a small amount of remaining molecular benzene, consistent with the TPD data shown in Figure 1.

By heating the monolayer to 470 K, all chemisorbed benzene desorbs or decomposes as indicated in Figure 2B by the complete disappearance of \(\nu(Rh-C)\) modes at 345 and 550 cm\(^{-1}\) for molecularly adsorbed benzene. Otherwise, this 470 K benzene decomposition spectrum is deceptively similar to that in Figure 2A for molecularly adsorbed benzene. The subtle changes in this fragment spectrum are more easily seen in Figure 3, which compares the specular and 20° off-specular HREEL spectra of this 470 K monolayer. These changes are detailed below:

(1) A new \(\nu(Rh-C)\) mode appears at 325 and 457 cm\(^{-1}\).

(2) An intense loss peak at 800 cm\(^{-1}\), largely due to CH bending modes, also characterizes the hydrocarbon fragments formed by benzene decomposition. Clearly this peak is due to more than one mode, since the width (138 cm\(^{-1}\)) of this peak is nearly three times that of the elastic peak (48 cm\(^{-1}\)). The off-specular spectrum in Figure 3B also shows that at least two modes contribute to this peak.

(3) A weak, broad loss centered at 1365 cm\(^{-1}\) is observed in both specular and off-specular spectra. In addition, weak peaks at 930 and 1155 cm\(^{-1}\) are observed in off-specular spectra. HREEL spectra taken for \(C_6D_6\) decomposition show that the peak at 1365 cm\(^{-1}\) is largely due to \(\nu(CC)\) modes of hydrocarbon fragments with intact C–C bonds.

(4) Two \(\nu(CC)\) modes at 2928 and 3008 cm\(^{-1}\) are observed. After heating the monolayer to 570 K, the intense 800-cm\(^{-1}\) loss peak is still present as shown in Figure 2C, but has narrowed to 65-cm\(^{-1}\) fwhm. Concomitantly, the 475-cm\(^{-1}\) peak disappears, the 1365-cm\(^{-1}\) peak broadens and shifts to lower frequency, and the \(\gamma(CH)\) peak at 3000 cm\(^{-1}\) narrows and shifts to higher frequency.

Finally, heating to 800 K desorbs all hydrogen from the surface, and the vibrational spectrum in Figure 2D appears almost featureless with only very weak and broad loss peaks centered at 630 and 1260 cm\(^{-1}\). This spectrum is almost identical with that of an ordered (12 \times 12) graphite overlayer shown in Figure 4 (also see ref 8). Since carbon dissolves into bulk Rh at 1100 K, a 600
The Langmuir dose of C₆D₆ was required to saturate the near surface region with carbon and to form this ordered graphite film at 1100 K.

The ν(CH) region (2800–3200 cm⁻¹) for the decomposition spectra in Figure 2 is shown in more detail in Figure 5. There are at least two ν(CH) peaks (not completely resolved) whose relative intensities change with temperature. The 2988-cm⁻¹ peak for molecular benzene is replaced at 470 K by peaks centered at 2928 and 3008 cm⁻¹, and with heating above 470 K, the intensity of the 2928-cm⁻¹ peak decreases more rapidly than that of the 3008-cm⁻¹ peak. The 2928-cm⁻¹ peak disappears by 570 K and a new peak appears at 3020 cm⁻¹. We interpret these spectra to mean that there are at least two different adsorbed species present on the surface at 470 K, whose relative populations change with temperature as more hydrogen desorbs and the average H/C stoichiometry of this monolayer is reduced. This interpretation is consistent with the behavior of the 800-cm⁻¹ peak, due primarily to δ(CH) modes, which sharpens by 73 cm⁻¹ concurrent with the disappearance of the 2928-cm⁻¹ peak by 570 K.

Haaland⁹ has reported very similar spectra of the ν(CH) region as a function of temperature in studies of benzene decomposition on Pt/Al₂O₃ catalysts using Fourier transform infrared spectroscopy. He concluded that two distinct species were formed: di-α- and π-bonded benzene. Our results rule out the presence of molecular benzene at these temperatures on Rh(111) in UHV, so our assignment of these peaks to decomposition products differs from the work of Haaland. While these two systems are certainly quite different, the similarity in the ν(CH) frequencies and in the intensity changes that occur with temperature indicate that any benzene decomposition on Pt/Al₂O₃ would complicate the previous interpretation of the supported Pt spectra.

A clue as to the nature of the benzene decomposition species was found in our studies of acetylene decomposition on Rh(111).² In Figure 6, we compare the vibrational spectra of C₂D₂ and C₆D₆ monolayers that were momentarily heated to 470 K. The high background at low energy in these spectra results from using a different HREEL spectrometer and a different electron beam energy than were used to obtain the rest of the spectra in this study. These spectra do establish that acetylene and benzene decompose

---

TABLE I: Observed Vibrational Frequencies of CH Species

<table>
<thead>
<tr>
<th>mode assignment</th>
<th>H$_2$Ru$_2$(µ$_2$CH)(CO)$_2$</th>
<th>Co$_2$(µ$_2$CH)(CO)$_2$</th>
<th>normal coordinate analysis</th>
<th>Rh(111)/C$_2$H$_4$*</th>
<th>W(110)/C$_2$H$_4$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν(CH)</td>
<td>2988 [w]</td>
<td>3041 (2258, 1.35) [m]</td>
<td>3045 (2263, 1.34) [m]</td>
<td>2928 (2200, 1.33) [m]</td>
<td>2930 [w]</td>
</tr>
<tr>
<td>δ(CH)</td>
<td>894 [vs]</td>
<td>850 (680, 1.25) [s]</td>
<td>852 (679, 1.25)</td>
<td>~930 (---) [w]</td>
<td>925 [vw]</td>
</tr>
<tr>
<td>ν$_i$(MC)</td>
<td>670 [m]</td>
<td>715 (697, 1.03) [m]</td>
<td>715 (694, 1.03)</td>
<td>~750 (720, 1.04) [m, sh]</td>
<td>581 [w, sh]</td>
</tr>
<tr>
<td>ν$_a$(MC)</td>
<td>427 [m]</td>
<td>417 (410, 1.01) [w, sh]</td>
<td>432 (393, 1.10)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Frequencies are in cm$^{-1}$; numbers in parentheses are (deuterated frequency, ν(CH)/ν(CD)). s, strong; m, medium; w, weak; v, very; sh, shoulder.

Oxton, ref. 12. *Howard et al., ref. 13. *This work. *Backx and Willis, ref. 15.

TABLE II: Observed Vibrational Frequencies of C$_2$H Species

<table>
<thead>
<tr>
<th>mode assignment</th>
<th>O$_2$(CO)(µ$_3$H-)(µ$_2$-CCH)°</th>
<th>Rh(111)/C$_2$H$_4$*</th>
<th>Pd(111)/C$_2$H$_4$*</th>
<th>Ni(111)/C$_2$H$_4$*</th>
<th>Pt(111)/C$_2$H$_4$*</th>
<th>Ni(111)/C$_2$H$_4$°</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν(CH)</td>
<td>3157 (2377, 1.13) [ms]</td>
<td>3008 (2250, 1.31) [m]</td>
<td>3000 (2240, 1.34) [m]</td>
<td>2990 (2275, 1.31) [m]</td>
<td>3000 [m]</td>
<td>2980 (2160, 1.38) [w]</td>
</tr>
<tr>
<td>δ(CH)</td>
<td>1534 (1496, 1.03) [ms]</td>
<td>1365 (1365, 1.00) [w]</td>
<td>1340 (1340, 1.00) [w, br]</td>
<td>1290 (1275, 1.01) [w, br]</td>
<td>1430 [w]</td>
<td>1300 (---) [vw]</td>
</tr>
<tr>
<td>ν$_i$(MC)</td>
<td>861 (714, 1.21) [m]</td>
<td>850 (600, 1.4) [m]</td>
<td>750 (545, 1.38) [s]</td>
<td>890 (725, 1.23) [s]</td>
<td>~800 [m]</td>
<td>790 (550, 1.44) [s]</td>
</tr>
<tr>
<td>ν$_a$(MC)</td>
<td>854 (709, 1.20) [m]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Frequencies are in cm$^{-1}$; numbers in parentheses are (frequencies for deuterated analogues, ν(CH)/ν(CD)). s, strong; m, medium; w, weak; br, broad. Doublets are reported by J. R. Shapley from spectra taken in a KBr pellet and are probably state-splitting effects. Evans and McNulty, ref. 14, and Shapley, J. R., unpublished results. *This work. *Kesmodel et al., ref. 18. *Sirosci et al., ref. 19. *Baro and Ibach, ref. 16. *Demuth and Ibach, ref. 17. *Spectra reassigned to C$_2$H previously attributed to CH.

To produce the same adsorbed species above 410 K on Rh(111). These data further suggest that the adsorbed species produced by benzene decomposition contain only one or two carbon atoms.

**B. Peak Assignments.** Combining the information from the vibrational spectra and the TPD spectra enables us to assign the vibrational peaks and identify which species are formed on the Rh(111) surface from among the many possible fragment species that could occur.

We consider first the vibrational spectrum of a benzene monolayer momentarily heated to 470 K. We noted in the previous section that (1) H/C ~ 0.6 at this temperature, (2) all modes attributed to molecular benzene have disappeared, (3) at least two species are present, and (4) these species most likely contain only one or two carbon atoms. Possible adsorbed species of this kind are C$_2$H, CH$_2$, CH$_3$, CH$_2$, C$_2$H$_2$, C$_2$H$_3$, C$_2$H$_4$, CH$_2$C$_2$,CH,H$_2$, CH$_2$CH$_3$, CH$_2$CH$_2$, and CH$_2$CH$_3$. The presence of species containing a CH$_2$ group can be ruled out since the scissors mode of a CH$_2$ group would cause peak losses at ~1400 and ~1000 cm$^{-1}$ in the undeuterated and deuterated spectra, respectively, which are not observed in our spectra. Species containing CH$_3$ groups are also absent, since these groups have characteristic vibrational modes at ~1030, ~1350, and ~1450 cm$^{-1}$ in undeuterated spectra and at ~730, ~950, and ~1025 cm$^{-1}$ in deuterated spectra. This enhances the possibility of the contributions of CH$_2$, CH$_3$, C$_2$H, and C$_2$H$_2$. The presence of acetylene (HC≡CH) can be ruled out, since this molecule begins to decompose below 300 K on Rh(111).

Furthermore, at least two "CH-containing" species are present from our previous analysis of the CH stretching region shown in Figure 5.

The vibrational spectra of benzene thermally decomposed on Rh(111) at 470 K can be assigned straightforwardly to a mixture of CH and CCH species. From isotopic shifts in the C$_2$H$_4$ and C$_2$D$_4$ decomposition spectra at 470 K, the losses at 800, 2928, and 3008 cm$^{-1}$ are identified as C–H vibrations and those at 475 and 1365 cm$^{-1}$ as RH–C and C–C vibrations. The 720-cm$^{-1}$ loss in the C$_2$H$_4$ decomposition spectrum (Figure 6) is probably also from a Rh–C or C–C mode, since no corresponding loss is observed around 1000 cm$^{-1}$ in the C$_2$H$_4$ decomposition spectrum. All peaks observed on-spectrally have substantial dipole scattering contributions as indicated by the reduced intensity of the losses in the off-spectrally HREEL spectrum in Figure 3B. Therefore, according to the surface dipole selection rule, the vibrational modes indicated by these peaks must have a net dynamic dipole perpendicular to the surface.

Specific peak assignments are made by comparison with IR spectra of CH and C$_2$H ligands in organometallic clusters and with HREEL spectra of hydrocarbon fragments on other metal surfaces. We rely particularly on IR spectra of three organometallic complexes: (1) a triruthenium cluster with triply bridging CH, (2) a triobalt cluster with triply bridging CH on which a normal coordinate analysis has been made, and (3) a triosmium cluster with a tilted ethynyl (C$_2$H$_2$) ligand. Ruthenium, cobalt, and osmium surround rhodium in the periodic table and osmium’s metallic radius is within 0.7% of rhodium’s. The vibrational frequencies are tabulated in Table I for CH ligands and in Table II for C$_2$H ligands, along with the frequencies observed for adsorbed CH and C$_2$H species on Rh(111) and other metal surfaces. The C$_2$H vibrational frequencies on Ni and Pt surfaces in Table II were originally assigned to a "tipped" CH species. However, recent assignments of C$_2$H species suggest that the Ni and Pt surface fragments are tipped C$_2$H rather than tipped CH.

---


(15) Shenley, J. R., unpublished data.


species, and we have reassigned these spectra accordingly. Also, an acetylide (C$_2$H) species has been observed on Ag(110), but the different vibrational frequencies for $v$(CH) [3250 cm$^{-1}$] and $\delta$(CH) [690 cm$^{-1}$] indicate a much different bonding interaction for this species on Ag than for any of the C$_2$H species in Table II. We now explain in detail our assignment of the vibrational spectra for benzene decomposition at 470 K on Rh(111).

For adsorbed CH, assuming bonding in a hollow site with C$_{2v}$ symmetry, only two modes should be dipole active and therefore have substantial intensity in the specular HREEL spectrum: $v$(RhC) and $v$(CH). We assign the lower frequency CH stretch observed at 2928 cm$^{-1}$ in our spectra to this species by analogy to the CH and C$_2$H cluster compounds. The $v$(RhC) peak is obscured in this C$_2$H$_4$ decomposition spectrum by CH bending vibrations in C$_2$H, but it is probably the peak at 720 cm$^{-1}$ in the deuteronated spectrum shown in Figure 6A. On the W(110) surface, as shown in Table I, vibrational spectra attributed to adsorbed CH species also show a CH bending mode, $\delta$(CH), at 925 cm$^{-1}$ as judged by deuteronium isotope shifts. Similarly, we assign the weak peak at $\approx$930 cm$^{-1}$ in the off-specular spectrum in Figure 3B to the dipole inactive $\delta$(CH) mode of adsorbed CH on Rh(111).

The presence of stronger dipole active $\delta$(CH) loss peaks of C$_2$H species makes it difficult to determine the intensity of the 930-cm$^{-1}$ mode in the specular spectra, but some intensity due to this mode may be responsible for part of the observed broadening of the 800-cm$^{-1}$ loss toward higher frequency.

For adsorbed C$_2$H, about half of all normal vibrational modes should be dipole active if the species is adsorbed in a geometry with C$_{2v}$ symmetry. The 3008-cm$^{-1}$ mode can be assigned as $v$(CH) and the 1365-cm$^{-1}$ mode as $\delta$(CC). We assign the 325- (off-specular) and 475-cm$^{-1}$ modes as dipole-inactive and dipole-active Rh–C skeletal modes, respectively, from among the five possible Rh–C stretches and deformations. For the same species on Ni(110), Ni–C modes are observed at 380 and 465 cm$^{-1}$. In the ethynyl (C$_2$H) cluster, possible CH bending modes have been observed at 1259, 860, and 760 cm$^{-1}$. The 1259-cm$^{-1}$ band is probably a combination band. We correlate these C$_2$H cluster frequencies with Figure 3 as follows: the 860- and 760-cm$^{-1}$ modes shift to $\approx$850 and $\approx$800 cm$^{-1}$ and occur together in the broad loss at 800 cm$^{-1}$, and the 1259-cm$^{-1}$ mode shifts to 1155 cm$^{-1}$ (observed in Figure 3B). If the C$_2$H fragment has C$_{2v}$ symmetry, then the in-plane (in the CCH plane) CH bend should be dipole active and the out-of-plane bend dipole inactive. We assign the losses at 800 and $\approx$850 cm$^{-1}$ seen in the off-specular spectrum in Figure 3B to these dipole-active and dipole-inactive CH bending modes, respectively. We assign the weak 1155-cm$^{-1}$ peak as a combination band of the 325- and either 800- or $\approx$850-cm$^{-1}$ modes.

This assignment of the 470 K benzene fragment spectrum to a mixture of CH and C$_2$H species is summarized for the specular HREEL spectrum in Figure 7. The relative intensities for the modes contributing to the 800-cm$^{-1}$ peak in the "deconvolution" were chosen to reproduce the observed spectrum. Most of the intensity in this broad 800-cm$^{-1}$ peak results from the unresolved dipole-active, in-plane $\delta$(CH) of C$_2$H ($\approx$800 cm$^{-1}$) and dipole active $v$(MC) of CH ($\approx$750 cm$^{-1}$). The weaker dipole-inactive, out-of-plane $\delta$(CH) of C$_2$H ($\approx$850 cm$^{-1}$) and dipole-inactive $\delta$(CH) of CH ($\approx$930 cm$^{-1}$) broaden the 800-cm$^{-1}$ peak toward higher frequency.

Comparison of the intensities of the CH stretch loss peaks in the 470 K vibrational spectrum taken 20 off-specular and shown in Figure 3B gives an estimate of the concentration ratio of CH and C$_2$H species on the surface. This intensity comparison is valid since "impact scattering" is the predominant scattering mechanism of vibrational modes in the off-specular direction, and these CH stretch modes should have similar impact scattering cross sections. In the 470 K fragment spectrum in Figure 3B, the CH/C$_2$H CH-stretch peak (2928/3008) intensity ratio is 0.40. This corresponds to a surface stoichiometry of H/C $\approx$ 0.6, nearly identical with the stoichiometry determined by TPD, supporting our assignment of the 470 K vibrational spectrum. It should also be noted that the CH/C$_2$H CH–bond peak (930/800) intensity ratio in Figure 3B is also consistent with this H/C stoichiometry.

By heating these 470 K benzene fragments to 570 K, the distinct vibrational features due to adsorbed CH and C$_2$H disappear as shown in Figure 2C. The most notable effects are the loss of the $v$(RhC) and $v$(CH) modes of adsorbed CH which causes a large reduction in the width of the peaks near 800 and 3000 cm$^{-1}$. A large decrease in the coverage of adsorbed C$_2$H is also indicated by the disappearance of the 1365-cm$^{-1}$ $v$(CC) mode, the disappearance of the $\delta$(RhC) modes at 325 and 475 cm$^{-1}$, and the shift of the $v$(CH) mode to higher frequency. We attribute the spectrum in Figure 2C to C$_2$H polymers with n $\approx$ 3, formed by condensation of both CH and C$_2$H species. We assign the 800-cm$^{-1}$ peak to the two CH bending modes, the broad 1290-cm$^{-1}$ peak to CC stretching modes, and the 3020-cm$^{-1}$ peak to the CH stretch of this C$_n$H$_m$ species. The average polymer chain length of three carbon atoms was determined from TPD data which indicate a stoichiometry of H/C = 0.3 at 570 K. These polymers are likely precursors to graphite formation.

The lack of any distinct peaks in the HREEL spectrum after heating to 800 K, the (1×1) LEED pattern, and the similarity of the 800 K HREEL spectrum to that of a graphite monolayer on Rh(111) imply that complete dehydrogenation leaves a carbonaceous residue composed of disordered C$_n$ (n $\geq$ 3) polymers on the surface. The very weak modes in the ordered, incommensurate graphite spectrum in Figure 4 could be due to similar species that exist as structural defects in the graphite monolayer. Isolated carbon atoms which typically have frequencies around 550 cm$^{-1}$ were not detected at any point in the benzene decomposition. The generally high background intensity from 0 to 1400 cm$^{-1}$ in all decomposition spectra is characteristic of carbon polymerization and has been reported by McBreen et al. (20) Waddill, G. D.; Kesmodel, L. L. Surf. Sci., submitted for publication.
Figure 8. Suggested surface geometries for CH and C₂H on Rh(111).

al. for ketene polymerization on Fe(110). Furthermore, the broad, high-temperature tail in the TPD from 500 to 700 K may be a signature for this polymerization. The width of this broad TPD peak decreases with decreasing initial benzene coverage, possibly because of decreased polymerization.

Discussion

1. Structural Models for the Benzene Decomposition Fragments. The correlation shown in Tables I and II between the vibrational frequencies on close-packed metal surfaces and in organometallic trinuclear clusters for CH and C₂H species suggests that the bonding geometries of these surface and cluster species may be similar. Analogous correlations have been successfully made between ethylidyne (C₂H) surface and cluster complexes using vibrational frequencies determined by HREELS and IR25 and bonding geometries determined by LEED and X-ray diffraction.26 In the case of CH and C₂H species, some related cluster geometries are known, but no surface geometries have yet been determined. (Only recently has an ordered structure been observed for any C₂H species—the (2×2) LEED pattern observed for C₂H on Ni(110).19) We briefly describe the geometries of these cluster complexes as models for C₂H fragments on metal surfaces.

The geometry of methylidyne (CH) trinuclear clusters has the carbon atom symmetrically bridging the three metal atoms.13 Presumably the C–H bond is perpendicular to the metal plane. The M–C bond lengths are the same as in analogous ethylidyne (C₂H) complexes and the same M–C force constants determined for ethylidyne22 successfully predict the M–C vibrational frequency of the methylidyne cluster.14 By analogy to these clusters and to surface ethylidyne species,22 we propose that the CH fragment on Rh(111) bonds in a threefold hollow site as shown in Figure 8A.

For the ethynyl ligand (C₂H), no cluster crystal structures have been determined. However, geometries have been determined by X-ray crystallography for analogous M₂C₂R complexes, where M, R = Fe, phenyl27 or Ru, butyl.28 These C₂R ligands are “tilted” relative to the metal plane and have C–C bond lengths of ~1.3 Å (compared to 1.2 Å in C₂H₄ and 1.33 Å in C₂H₂). The ν(C≡C) frequencies for both the C₂H₂ cluster (1534 cm⁻¹) and the C₂H₄ surface species (1290–1365 cm⁻¹) are consistent with a C–C bond order of between 1 and 2. On the basis of the M₂C₂R cluster geometries, the C–C bond in the C₂H₄ surface species probably makes an angle of ~75° with the surface normal. The suggested geometry is shown in Figure 8B. Similar tilted surface geometries for C₂H₄ have been previously proposed based on UPS data on Ni(100) and Ni(110)29 and HREELS data on Ni(110).19 Molecular orbital calculations have been performed to predict the bonding geometry of CH and C₂H species on a Pt(111) surface.30,31 Minot et al.32 determined, using extended Hückel theory, that CH bonds in threefold hollow sites as opposed to top or bridge sites, in agreement with our proposed geometry on Rh(111). Calculations on the bonding of C₂H on Pt(111) by Minot et al.32 and Kang and Anderson43 lead both groups to conclude that C₂H should bond as a linear acetylide (C–CH) at a top site with the colinear C–C–H axis along the surface normal. This geometry differs from our proposed C₂H geometry on Rh(111), but our proposed geometry (Figure 8B) was not considered in either of the molecular orbital calculations. Thus, it would be important to carry out additional calculations on C₂H bonding with a nonlinear geometry in a threefold hollow site. We note, however, that linear C₂H bonding at a top site is consistent with the C₂H vibrational spectrum on Ag(110)44 where ν(CH) = 3250 cm⁻¹, as expected for sp-hybridized carbon. It is interesting to follow the frequency shift, broadening, and decrease in intensity that occur with increasing temperature for the ν(C≡C) loss peak as the composition of the hydrocarbon monolayer changes from C₆H₆ + CH to a carbonaceous residue. As shown in Figure 2 this peak broadens and shifts from 1365 cm⁻¹ for C₆H₆ (Figure 2B) to ~1290 cm⁻¹ for C₂H (Figure 2C) and to ~1260 for C₆H₆ at 800 K (Figure 2D). These frequency and intensity changes are characteristic of carbon polymerization on metal surfaces.45 Polymerization broadens the ν(C≡C) peak for two reasons: (1) C–C bonds in carbon polymers are coupled, resulting in many normal modes with different vibrational frequencies that are not resolved at 50-cm⁻¹ resolution and (2) differences in bonding geometries and in carbon chain lengths result in polymerization, again resulting in a large number of unresolved vibrational frequencies. In addition to peak broadening, polymerization is likely to decrease the intensity of the ν(C≡C) peaks by forcing CC bonds to be more nearly parallel to the metal surface and thus have weaker dipole scattering. Additional studies of these weak ν(C≡C) vibrations at 1200–1400 cm⁻¹ may provide insight into the microscopic details of graphite formation on metal surfaces.

II. Benzene Decomposition Pathway. We have shown that when benzene decomposes on Rh(111) at 400 K the decomposition fragments (CH and C₂H) are the same as for decomposed acetylene at this temperature. This suggests, as shown in Figure 9, that benzene decomposes at 400 K by C–C bond scission to give three acetylenes as intermediates which immediately decompose to CH and C₂H species. Indeed, high coverage acetylene TPD spectra on Rh(111)50 show similar H₂ desorption peak positions and integrated areas to those found for benzene.

As discussed below, further support for the proposal that acetylene is an intermediate in benzene decomposition over Rh surfaces comes from LEED, Raman spectroscopy, H₂ exchange studies, and comparison to other metal/hydrocarbon systems. Dynamical LEED calculations52 indicate that chemisorbed benzene, when coadsorbed with an equivalent amount of CO, on Rh(111) bonds in a threefold hollow site and desorbs to a structure with alternating short and long C–C bond lengths of 1.33 and 1.81 Å. The C–C bond length of 1.33 Å is consistent with that of gas-phase acetylene (1.40 Å) toward that of gas-phase acetylene (1.20 Å). Also, Raman spectroscopy studies of Rh/Al₂O₃ show that at room temperature chemisorbed benzene can be induced to decompose to acetylene by introducing a strong π acceptor ligand like CO or NO.31

Several other observations support the proposal that C–C bond breaking initiates the decomposition of benzene on Rh. Heating benzene adsorbed on Rh(111) to 400 K in a background of deuterium never gave any evidence of deuterium exchange in the HREEL spectra. This is analogous to TPD studies on Ni(111), -(100), and -(110)33 and Pt(111)35 using C₂H₄ + D₂ and C₂H₂ + C₂D₆ where no partially deuterated benzene was found to desorb in the molecular decomposition peak. By contrast, straight-chain alkenes on Pt(111),34 benzene on Pt(100),35 and benzene on

References

Figure 9. Proposed pathway for benzene decomposition on Rh(111).

stepped Pt[6(111)×(111)] desorb highly deuterated when coadsorbed with D2, and benzene H,D exchange is observed in HREEL spectra on Pt(100) and Pd(111). Furthermore, straight-chain alkenes decompose by CH bond scission at a much lower temperature than benzene on Rh(111): 200 K vs. 400 K. The implication is that benzene decomposition may be initiated by C=C bond scission on Rh(111) and Ni where no H,D exchange is observed, while C-H bond scission may occur first on Pd(111) and some Pt surfaces where H,D exchange occurs.

Data from the literature suggest that a delicate balance exists between the stability of benzene and that of three acetylenes on metal surfaces. Ni(111) is not reported to form benzene from acetylene in UHV, but Ni on SiO2 catalyzes acetylene trimerization at atmospheric pressure.37 Rh(111), like Ni(111), does not form benzene from acetylene in UHV, with or without coadsorbed CO.38 No studies on acetylene trimerization at atmospheric pressure over Rh(111) have been reported. Benzene chemisorbed with CO distorts toward three acetylenes on Rh(111)39 and decyclotrimerizes to three acetylenes on Rh/Al2O3.40 By contrast, Pd trimerizes acetylene both in UHV39,40 and at 1-atm pressure.41 In solution, trimerization is favored over decycloreimerization, and rhodium trinuclear complexes perform acetylene trimerization with fairly high yield.42

Finally, it should be recognized that the benzene decomposition pathway and stable surface fragments that we observe on Rh(111) in ultrahigh vacuum may be entirely different from those under catalytic reaction conditions. Hydrocarbon fragment stability is affected by the surface H atom concentration which is determined by the ambient H2 pressure. Our studies in ultrahigh vacuum favor dehydrogenation accompanied by hydrogen desorption, while catalytic hydrocarbon conversion reactions are carried out in high pressures of H2, increasing the stability of hydrogenated surface fragments.

Conclusions

The chemisorption of benzene on Rh(111) is largely irreversible, molecular desorption accounting for less than 15% of the benzene adsorbed at saturation coverage. Thermal decomposition of benzene starts at 400 K on Rh(111) in ultrahigh vacuum. The adsorbed decomposition products formed are independent of both the initial benzene adsorption site and whether or not coadsorbed CO is present. The stable surface species formed between 400 and 500 K are CH and C2H, and at 470 K the ratio C2H:CH is 2.5. No ordered LEED patterns were found for any of the decomposition products.

Model organometallic cluster compounds, which exhibit similar vibrational frequencies to these CH and C2H species on Rh(111), lead us to propose that adsorbed CH bonds in a threefold hollow site on Rh(111) with the CH bond along the surface normal, while adsorbed C2H bonds with the CC bond at an angle of ~75° from the surface normal and with a CC bond order of between 1 and 2. Above 500 K, these CH and C2H fragments dehydrogenate and polymerize to form CnHx species, with complete dehydrogenation and formation of Cn polymers by 800 K. Based on these data, we propose that benzene decomposition on Rh(111) occurs by decycloreimerization initiated by CC bond scission, and that acetylenic species are unstable intermediates during this process.

Acknowledgment. The experimental work was done at the University of California, Berkeley, and was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DEAC03-76SF00098. We gratefully acknowledge helpful discussions with Professor J. R. Shapley and Dr. F. Zaera, and we thank Prof. Shapley for supplying IR data on Os6(CO)12(μ-H)(μ3-CH3)(μ-η2-CCH) prior to publication. B. E. Koel acknowledges the partial support of the Miller Institute for Basic Research in Science, the Camille and Henry Dreyfus Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. B. E. Bent gratefully acknowledges a National Science Foundation Fellowship; and C. M. Mate gratefully acknowledges a scholarship from the American Vacuum Society.

Registry No. Rh, 7440-16-6; benzene, 71-43-2.