

Investigation of an Alternative Reaction Pathway in the Cyclization of Ethyne to Benzene on Palladium: Cyclooctatetraene on Pd(111)

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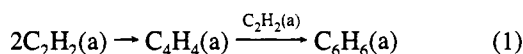
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Received February 21, 1995[⊗]

Abstract: Cyclooctatetraene (COT) to benzene conversion can be induced on Pd(111) under conditions of (low) temperature and overlayer density similar to those that obtain during the trimerization of ethyne to benzene. Coadsorbed NO inhibits COT decomposition, but does not increase its reactivity; HREELS shows that COT drastically affects NO site occupancy. Coadsorbed C₆D₆ both inhibits decomposition and strongly enhances the reactivity of COT: almost 100% COT → benzene selectivity can be achieved. A consistent interpretation of the vibrational spectra and reactivity is given: flat-lying COT undergoes decomposition, μ^4 *tub*-COT is unreactive, μ^4 *chair*-COT is reactive. This explanation takes account of the effects of metal-mediated charge transfer on the geometry of adsorbed COT. C₄H₄ cannot be induced to undergo coupling to COT, even in the presence of C₆D₆ or NO, both of which strongly promote ethyne-to-benzene conversion. It is therefore argued that C₂H₂ → C₄H₄ → C₈H₈ → C₆H₆ (+C₂H₂) cannot be a major pathway in ethyne cyclization.

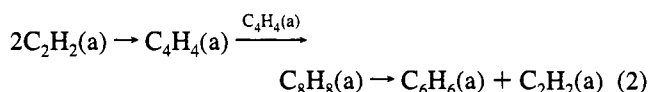
Introduction

Heterogeneously catalyzed ethyne to benzene cyclization over Pd surfaces is an efficient low-temperature reaction which has been extensively studied from a mechanistic point of view.¹ The process is particularly interesting because it can be operated under widely different conditions: single crystals under ultrahigh vacuum and dispersed Pd catalysts at atmospheric pressure² are both effective. Earlier work has shown that the reaction involves an associative mechanism³ with an adsorbed C₄ metallocycle as the key intermediate. The proposed route is



The structure and bonding of C₄H₄ on Pd(111) have been characterized in some detail (HREELS,⁴ NEXAFS⁵), as have the properties of the adsorbed reactant and product species.^{6,7} In the present connection, the following observations are pertinent: (i) ethyne may also be cyclized over Ni powder⁸ leading to *co-production of benzene and cyclooctatetraene*

(COT); (ii) Hostetler *et al.* have recently demonstrated that ring contraction of COT to benzene (+ethyne) is a characteristic reaction of the Pt(111) surface;⁹ (iii) Sn-doped Pt(111) also produces benzene from ethyne.¹⁰ Given that Sn moderates the C–H bond breaking activity of Pt, thereby making it more “Pd-like”, a very possible alternative pathway to benzene formation on palladium(111) is *via* COT as intermediate, thus



Recent *ab initio* calculations¹¹ indicate that eqs 1 and 2 are associated with comparable stabilization of the intermediates and products with respect to the reactants, so that the latter route does indeed deserve detailed consideration, especially as both equations are consistent with the results of our isotope tracing studies.³ In addition, eq 2 could account for the formation³ of some C₆H₆ when reaction is induced in a mixed layer of C₂D₂-(a) and C₄H₄(a) on Pd(111) at high C₄H₄(a) relative coverage (according to eq 1, the only products should be C₆D₆ and C₆H₄D₂).

Here we report an investigation aimed at assessing the importance or otherwise of a COT-mediated pathway in the cyclization of ethyne to benzene over Pd(111). Dissociative chemisorption of *cis*-1,4-dichlorocyclobutene (DCB) was used for dosing the metal surface with C₄H₄(a),³ and temperature-programmed reaction/desorption measurements were carried out on the following systems: COT; COT + C₆D₆; COT + NO; DCB; DCB + NO. It is found that chemisorbed COT does indeed undergo extensive conversion to benzene on Pd(111). However, the results also indicate that in the conversion of ethyne to benzene over Pd, eq 2 represents no more than a minor channel; eq 1 is confirmed as the predominant route.

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[⊗] Abstract published in *Advance ACS Abstracts*, July 1, 1995.

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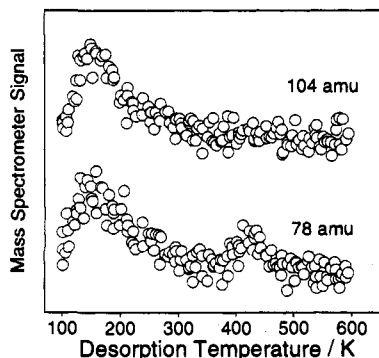


Figure 1. Temperature-programmed reaction spectra following a 3 L COT exposure on Pd(111) at 150 K.

Experimental Section

Experiments were carried out in two ultra-high-vacuum chambers^{12,13} operated at base pressures of $<1 \times 10^{-10}$ Torr. The Pd(111) sample could be resistively heated to 1200 K and cooled to 80 K. It was cleaned by Ar^+ etching ($500 \text{ eV}/6 \times 10^{-2} \text{ A m}^{-2}$) until LEED/AES indicated a well-ordered surface, free of contaminants. The C (270 eV) Auger peak overlaps with a major Pd Auger transition, therefore oxygen treatment (800 K, 1×10^{-8} Torr) followed by thermal desorption was used to check for the absence of surface C—diagnosed by subsequent desorption of O_2 , in the absence of CO and CO_2 . Chlorine deposited during DCB adsorption was removed by flashing to 1100 K. Low adsorbate coverages were achieved by backfilling the chamber ($<2 \times 10^{-8}$ Torr) and a quartz capillary array doser was used to attain higher coverages (gain factor ~ 15). Gas dosing was carried out at 150 K unless otherwise stated. Research grade NO (Distillers 5.0) was used without further purification; the hydrocarbons (COT 98%, C_6D_6 99%, $\text{C}_4\text{H}_4\text{Cl}_2$ 99%—Aldrich) were purified by repeated freeze–pump–thaw cycles. Quoted exposures are in Langmuirs ($1 \text{ L} = 10^{-6} \text{ Torr s}$) and are uncorrected for ionization gauge sensitivity. For TPD/TPR measurements the sample was positioned ~ 4 cm from the mass spectrometer ionizer such that $>90\%$ of the detected signal arose from the front face; the heating rate was 5–7 K/s. HREELS experiments were carried out on a VSW ARIES chamber also equipped with XPS and a VG Q7 quadrupole mass spectrometer. The primary beam energy was 9.8 eV. The beam was incident on the sample at an angle of 45° and all measurements were made in specular geometry using a HAC 300 analyzer with single channel detector. A resolution of $\sim 80 \text{ cm}^{-1}$ fwhm was routinely achieved.

Results

Temperature-Programmed Reaction. (a) Cyclooctatetraene on Pd(111). For exposures <1 L, TPD gave hydrogen as the only detectable product desorbing in a single peak between 600 and 700 K. Higher exposures led to the onset of COT desorption (104 amu, C_8H_8^+) principally in a peak centered around 180 K; assuming first-order desorption kinetics this corresponds to a desorption activation energy of only $\sim 45 \text{ kJmol}^{-1}$;¹⁴ this feature attained its limiting intensity after a 4 L COT dose. For higher doses, continuous growth of a lower temperature feature (~ 150 K) indicated the onset of multilayer formation, which is not of interest here. COT also yields ions at 78, 52, and 26 amu, as does benzene. The 78-, 52-, and 26-amu spectra deviate increasingly from the 104-amu spectra for COT doses above 1.5 L. In particular, the former exhibit growth of a new feature at ~ 500 K: this shifts to lower desorption temperatures with increasing exposure, reaching maximum intensity and a peak temperature of ~ 400 K after a 3 L COT exposure (Figure 1).

The 78:52 intensity ratio associated with the high-temperature feature enabled us to associate it with *desorption of reactively-formed benzene*. XPS measurements of the C 1s peak recorded before and after flashing a saturated COT adlayer to 600 K reveal that $\sim 40\%$ of carbon atoms do not desorb during the TPD ramp. Correcting for the mass spectrometer sensitivity toward COT and benzene, we thus obtain a maximum degree of $\text{COT} \rightarrow \text{benzene}$ conversion (X) of $\sim 35\%$ under these conditions, where

$$X = \frac{\text{mol of } (\text{C}_6\text{H}_6)}{\text{mol of } (\text{COT})_{\text{adsorbed}}}$$

and $\text{mol of } (\text{COT})_{\text{adsorbed}} = 1.66\{\text{mol of } (\text{C}_6\text{H}_6) + \text{mol of } (\text{COT})_{\text{desorbed}}\}$. No C_2 desorption products were observed under any conditions, suggesting that ethyne eliminated during $\text{C}_8 \rightarrow \text{C}_6$ ring contraction undergoes decomposition, contributing to surface carbon deposition. Accurate benzene yield measurements were not possible for COT doses >4 L because in this regime the 78- and 52-amu contribution from the COT multilayer desorption peak interferes with the 78- and 52-amu signals from the benzene peak which now occurs at ~ 250 K. No ordered adsorbate structures were observed by LEED for any COT coverage.

(b) Co-adsorption of Cyclooctatetraene and C_6D_6 on Pd(111). These measurements permit one to determine whether ring contraction of adsorbed COT *or* desorption of the benzene product is rate controlling for appearance of benzene in the gas phase. Both possible adsorption sequences were examined: COT followed by benzene and *vice versa*. Calibration experiments with C_6D_6 showed that the C_6D_3^+ intensity (78 amu) was $<5\%$ that of the parent ion (C_6D_6^+); therefore changes in the 78-amu TPD/TPR spectra may be attributed to production of reactively-formed C_6H_6 .

In the first set of co-adsorption experiments, TPD/TPR spectra were taken from a surface pre-dosed with 3 L of COT, then subjected to varying doses of C_6D_6 . (A 3 L COT pre-dose was chosen to maximize the yield of reactively-formed benzene desorbing at ~ 400 K.) The only desorption products detected were COT, C_6D_6 , and C_6H_6 . The absence of ethene and ethane indicates that the cyclic hydrocarbons undergo very little decomposition.

In marked contrast with the behavior found in the absence of COT where complete decomposition of the molecule occurs,¹⁵ benzene- d_6 doses as low as 0.05 L resulted in some C_6D_6 desorption at ~ 500 and ~ 200 K, associated with flat-lying and tilted benzene molecules, respectively.^{3,16,7} Increasing C_6D_6 exposure led to efficient population of the 200 K (tilted) state: by 0.5 L desorption from this state dominated, again contrasting with the behavior in the absence of COT, where only the 500 K peak would appear under these conditions. The C_6D_6 uptake saturated at 2 L exposure. The effects of co-adsorbed C_6D_6 on the yield and kinetics of $\text{COT} \rightarrow \text{C}_6\text{H}_6$ conversion are revealing. Firstly, even a very small dose of co-adsorbed C_6D_6 is sufficient to dramatically increase the yield of reactively-formed benzene, which saturates after only 0.5 L of C_6D_6 . The desorption yields of C_6D_6 and COT rise progressively more slowly than that of C_6H_6 with increasing C_6D_6 exposure only saturating after 2 L of C_6D_6 . Secondly, the C_6H_6 TPR spectra are closely correlated with the corresponding C_6D_6 TPD spectra (Figure 2a). This is a clear indication that desorption of reactively-formed C_6H_6 is rate limiting for the appearance of the gaseous product, i.e. the preceding cycloreversion/ring-contraction surface reaction is *not* rate controlling.

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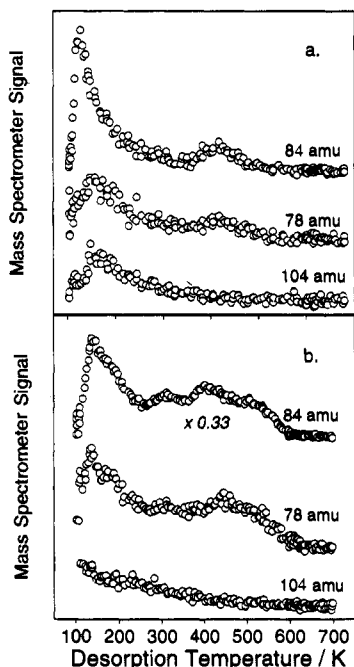


Figure 2. Temperature-programmed reaction spectra following the sequential coadsorption of (a) 3 L COT + 2 L C_6D_6 and (b) 2 L C_6D_6 + 2 L COT, on Pd(111) at 150 K.

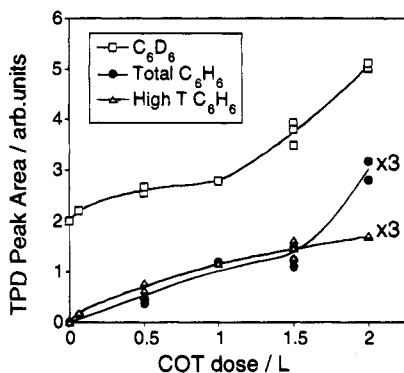


Figure 3. Variation in desorption yield of C_6D_6 and reactively-formed C_6H_6 from a Pd(111) surface precovered by 2 L of C_6D_6 as a function of subsequent COT exposure at 150 K.

Reversing the dosing procedure yields similar results. Increasing doses of COT on a surface pre-dosed with 2 L of C_6D_6 results in the progressive appearance of C_6D_6 TPD features resembling those associated with higher coverages of adsorbed benzene on a COT-free surface. Thus for a 2 L COT dose, the C_6D_6 TPD spectrum is characteristic of benzene-saturated Pd(111),¹⁵ with four distinct peaks observed between 200 and 500 K (Figure 2b). The data in Figure 4 also indicate that *conversion of COT to C_6H_6 now occurs with essentially 100% efficiency* (suppression of the 104 amu spectrum). Comparison with the data for a 2 L COT dose on clean Pd(111) shows that the presence of co-adsorbed C_6D_6 results in >500% growth in the yield of reactively-formed C_6H_6 , a substantial amount of which desorbs below 200 K. Detailed analysis of the various desorption features as a function of COT coverage (Figure 3) reveals that the initial rise in C_6H_6 yield is principally due to molecules which desorb above 300 K. These high temperature C_6H_6 features saturate at ~1.5 L COT exposure, additional COT reacting to form more weakly bound C_6H_6 . Similarities in the coverage dependence of the C_6D_6 and total C_6H_6 desorption yields are also apparent—both quantities increase in two stages. Again, we see that high total adsorbate density strongly promotes the cycloreversion reaction of COT to benzene. The sharp rise in C_6D_6 yield above 1 L of COT indicates that on clean Pd-

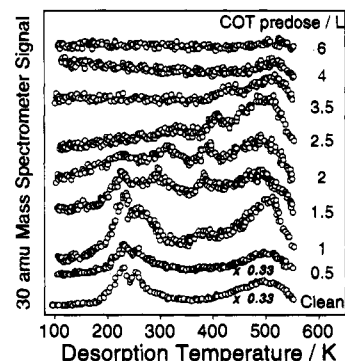


Figure 4. NO temperature-programmed desorption spectra following a 4 L NO exposure on Pd(111) as a function of COT precoverage at 150 K. Clean surface desorption for 4 L of NO is shown for comparison.

(111) chemisorbed benzene undergoes extensive decomposition, an amount equal to ~50% of the maximum uptake being lost by this route. As with COT alone on Pd(111), no new LEED patterns were observed under any conditions when COT and C_6D_6 were coadsorbed.

(c) **Coadsorption of Cyclooctatetraene and NO.** Ethyne cyclization is a structure-sensitive reaction whose efficiency is very strongly influenced by both surface crystallography and packing density of the reactant.^{17,18,19} Given that compression of the reactant phase by co-adsorbed NO dramatically promotes ethyne cyclization on Pd(111)¹³ and that the configuration of adsorbed reactant and intermediate species is important in benzene production from COT on Pt(111),⁹ we investigated the effect of NO on the properties of COT overlayers. The NO molecules behave as unreactive spectator species which may alter the chemistry by affecting the proximity of reactive hydrocarbon species.^{13,15}

Dosing a COT-precovered surface with 4 L of NO had no significant effect on the subsequent desorption/reactive behavior of the hydrocarbon over the whole range of COT coverage (4 L of NO corresponds to a saturation dose on clean Pd(111)). The 104- and 78-amu spectra evolved as in the case of COT adsorption alone. This is as expected by comparison with coadsorption experiments using C_6H_6 and NO, where strong binding of the preadsorbed hydrocarbon appears to preclude its subsequent perturbation by NO. However, very major changes are observed in the NO desorption as illustrated in Figure 4 which also shows desorption spectra of NO from clean Pd(111).

In particular, the presence of COT coverages >1 L leads to the development of four clearly resolved peaks and results in a progressive overall shift of NO desorption toward higher temperatures. On clean Pd(111) the 250 and 500 K desorptions arise from atop and 2-fold bridging NO molecules, respectively.^{20,21} (Recall that 1 L COT exposure corresponds to the threshold coverage for benzene formation.) Thus the presence of pre-adsorbed COT has a profound effect on the behavior of subsequently adsorbed NO; the COT itself remains essentially unaffected.

Reversing the order of adsorption resulted in significantly different behavior: varying pre-coverages of NO were followed by a fixed (1 L) dose of COT. The latter was chosen to be just below the threshold coverage required for COT desorption and benzene formation on clean Pd(111). Low pre-coverages of

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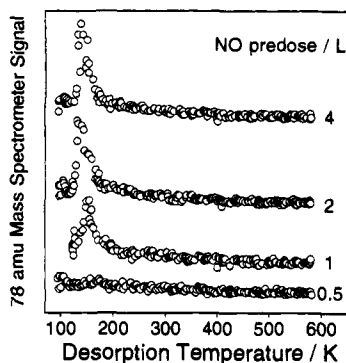


Figure 5. 78-amu temperature-programmed desorption spectra following a 1 L COT exposure on Pd(111) as a function of NO pre-coverage at 150 K.

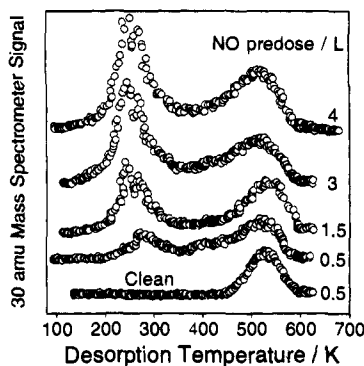


Figure 6. NO temperature-programmed desorption spectra following a 1 L COT exposure on Pd(111) as a function of NO pre-coverage at 150 K. Clean surface desorption for 0.5 L of NO is shown for comparison.

NO (<1 L) prior to the 1 L COT dose did result in COT desorption *below* the threshold COT exposure required on clean Pd(111). This appeared in the 78- and 104-amu signals as a single, weak peak at ~200 K (Figure 5). For NO pre-coverages >1 L this low-temperature 78/104 amu desorption peak grew rapidly with increased NO dose, shifting down to ~150 K. It saturated at 4 L NO pre-coverage, resembling the 150 K desorption obtained with 6 L of COT on clean Pd(111). Despite this strong perturbation of the COT, no reactively-formed benzene was observed for any NO pre-coverage. Furthermore, in contrast with the reverse dosing sequence, the corresponding NO spectra only deviate from those obtained with NO alone on Pd(111) for low NO pre-coverages (<1.5 L). Thus two desorption features at 250 and 500 K were apparent over the range of 1.5 to 4 L of NO, together with the associated $c(4 \times 2)$ and (2×2) LEED patterns. Even NO pre-coverages <1.5 L are only weakly compressed by COT, manifest as a shift from a $c(4 \times 2)$ LEED pattern to a diffuse (2×2) pattern, and early appearance of the 250 K NO desorption (Figure 6). These findings agree generally with the behavior of the NO + C₆H₆ system, where preadsorbed NO strongly compresses C₆H₆, but is itself only weakly perturbed.¹⁵

(d) Coadsorption of *cis*-3,4-Dichlorocyclobutene and NO on Pd(111). It has been shown³ that dissociative chemisorption of *cis*-3,4-dichlorocyclobutene (DCB) on Pd(111) yields high surface concentrations of the critical intermediate C₄H₄. As noted above, quantum chemical calculations¹¹ on finite Pd clusters are in good agreement with the experimentally determined structure, bonding, and relative energies of C₂H₂, C₄H₄, and C₆H₆ on Pd(111). These calculations also show that on this surface C₈H₈(a) is energetically favored with respect to 2C₄H₄(a). Given that the coupling of adsorbed ethyne is critically dependent on intermolecular separation and that this process can be promoted by compressing the hydrocarbon phase

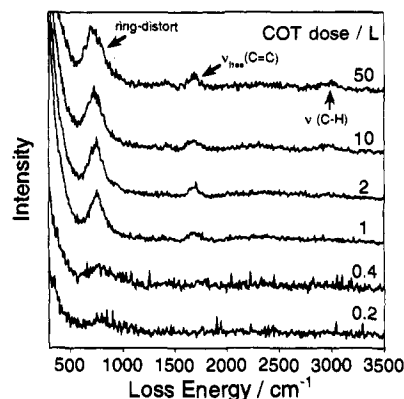


Figure 7. HREELS spectra as a function of COT exposure on clean Pd(111) at 150 K.

with co-adsorbed NO¹³ we investigated whether coupling of two C₄H₄(a) to C₈H₈(a) could be similarly promoted by NO(a). Low doses of DCB on Pd(111) at >150 K lead to dissociative chemisorption³



and the chlorine adatoms do not participate in subsequent reactions. For present purposes, the optimum DCB dose was found to be 0.4 L (higher exposures lead to the onset of multilayer formation). As before, both adsorption sequences were investigated. The results clearly indicate that NO(a) progressively compresses preadsorbed DCB layers, increasingly inhibiting dissociation of the latter. When NO was preadsorbed, subsequently deposited DCB could be dissociated by controlled heating to temperatures >150 K; this was manifested by a monotonic decrease in the amount of molecular DCB desorption. However, the resulting C₄H₄(a) + NO(a) system could not be induced to produce either C₆H₆(g) or C₈H₈(g). The principal effect of subsequent heating was decomposition to surface carbon and gaseous hydrogen with some desorption of molecular DCB. Attempts to induce reaction between adsorbed C₄H₄ molecules by using C₆D₆ to compress the hydrocarbon layer were also unsuccessful. Since C₄H₄(a) reacts very efficiently with C₂H₂(a) to yield C₆H₆(g) under these conditions³ we conclude that the coupling of two C₄H₄(a) species is inhibited by limited surface mobility and/or the presence of a significant activation barrier to reaction.

HREELS. (a) Cyclooctatetraene on Pd(111). The adsorption of COT doses >1 L at ~150 K resulted in the appearance of a single, broad loss feature at 770 cm⁻¹. This peak sharpened and shifted downward to ~720 cm⁻¹ with increasing COT exposure, while two weak features emerged at 1420 and 2960 cm⁻¹, together with a more intense loss at 1680 cm⁻¹ (Figure 7). Comparison with the COT liquid-phase IR spectrum²² and the HREELS assignments for COT on Pt(111) suggests the COT losses correspond to the following modes: ring distortion, ~750 cm⁻¹; $\nu(\text{C}=\text{C})$, 1680 cm⁻¹ (unbound); $\nu(\text{C}-\text{H})$, ~3000 cm⁻¹. The intensities of the three principal losses increased slightly with COT dose, saturating above 4 L; the corresponding energies were independent of COT coverage. There was no clear evidence of benzene formation at 150 K, although the principal benzene losses at ~750, 1410, and 2940 cm⁻¹ may be obscured by COT spectral features.

(b) Coadsorption of Cyclooctatetraene and C₆D₆. The sequential coadsorption of 2 L of C₆D₆ followed by saturation COT was performed at 150 K to investigate whether reactively-formed C₆H₆ could be detected on the surface below 200 K, as might be expected in light of the corresponding TPR results

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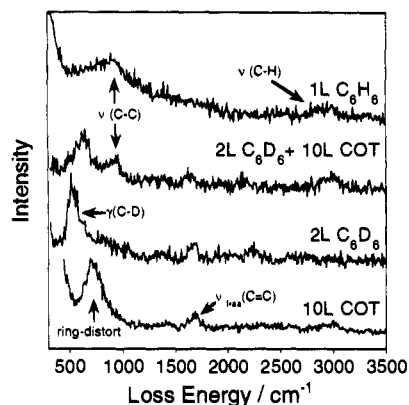


Figure 8. HREELS spectra following sequential coadsorption of 2 L of C_6D_6 + 10 L of COT on clean Pd(111). Comparative clean surface spectra are shown for 1 L of C_6H_6 , 2 L of C_6D_6 , and 10 L of COT.

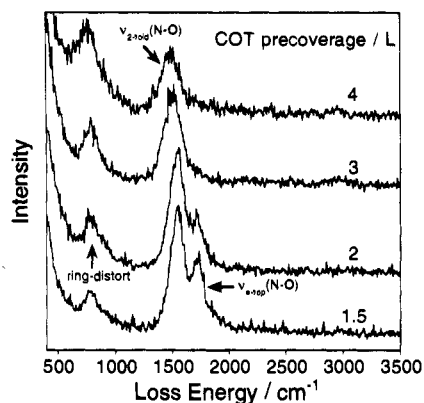


Figure 9. HREELS spectra for a 4 L NO exposure on Pd(111) as a function of COT pre-coverage at 150 K.

described above. Standard HREELS spectra for 2 L of C_6H_6 and 2 L of C_6D_6 on clean Pd(111) were also recorded at 150 K. The spectrum for low C_6H_6 coverages exhibits loss features at 940 and 2940 cm^{-1} ; the principal loss features for 2 L of C_6D_6 occur at 520 and 1680 cm^{-1} .

Following a saturation COT exposure on a surface predosed with 2 L of C_6D_6 , strong loss peaks were observed at 680, 940, 1650, and 3000 cm^{-1} (Figure 8). A weak shoulder at 520 cm^{-1} may be assigned to the C_6D_6 $\gamma(C-D)$ wag mode, while the sharp feature at 680 cm^{-1} arises principally from COT ring deformation. Both C_6D_6 and COT may contribute to the loss at 1650 cm^{-1} , while the peak at 3000 cm^{-1} may arise from either COT or C_6H_6 . However, the feature at 940 cm^{-1} corresponds to the $\nu(C-C)^{23,24}$ mode of C_6H_6 and cannot be assigned to any C_6D_6 or COT mode. *This provides clear evidence for the presence of reactively-formed C_6H_6 at <200 K.*

(c) **Coadsorption of Cyclooctatetraene and NO.** The unusual NO desorption features resulting from the low-temperature, sequential coadsorption of COT and NO prompted a vibrational analysis of this system. Information on the NO adsorption sites is of particular interest. HREEL spectra shown in Figure 9 were recorded for varying pre-coverages of COT ($\sim 1-4$ L), followed by a saturation dose of NO (>4 L) at 150 K. For COT pre-doses <1.5 L, strong loss features appeared at 780, 1550, and 1720 cm^{-1} . The relative intensity of the N-O modes at 1550 and 1720 cm^{-1} was $\sim 1:0.5$ for 1.5 L of COT. For comparison, saturation NO coverage on clean Pd(111) gives losses at 1580 and 1740 cm^{-1} with a very different intensity

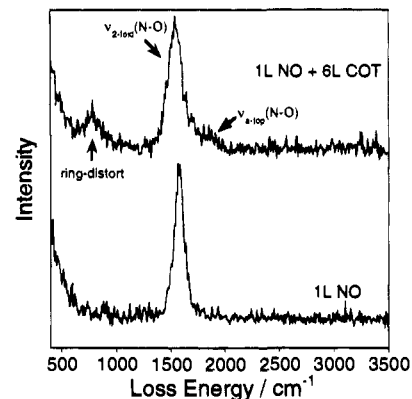


Figure 10. HREELS spectra for a 6 L COT exposure on Pd(111) precovered by 1 L of NO. Clean surface spectra for 1 L of NO are shown for comparison.

ratio, namely 1:2. (The 1550- and 1720- cm^{-1} losses correspond to NO molecules in a 2-fold bridge and atop sites, respectively²⁰). Increasing the COT pre-coverage (>2 L) suppressed the 1720- cm^{-1} loss, eventually extinguishing it; the 1550 cm^{-1} loss had shifted down to ~ 1490 cm^{-1} with 4 L of COT. The 780- cm^{-1} feature was both coverage and temperature independent.

Pre-dosing Pd(111) with 1 L of NO at 150 K gave rise to a single loss at 1580 cm^{-1} (Figure 10). Subsequent saturation with COT at 150 K shifted this feature to ~ 1540 cm^{-1} and induced a new, weak shoulder at ~ 1800 cm^{-1} .

Discussion

At low coverages, the XPS and TPR data show that COT chemisorbed on Pd(111) undergoes decomposition when surface temperature is raised: carbon and gaseous hydrogen are the only products. The absence of $\nu_{C=C}$ and ν_{C-H} modes from the HREELS data for such low-density chemisorbed layers is consistent with a flat-lying geometry for the adsorbed molecule. It might be expected that such a strongly interacting species would tend to undergo decomposition on the metal surface. At higher coverages the vibrational spectra clearly indicate that the molecule undergoes a substantial change in adsorption geometry which is accompanied by the appearance of an unbound $C=C$ stretch at 1680 cm^{-1} and a $C-H$ stretch at 3000 cm^{-1} . In this configuration, decomposition of the molecule is reduced and benzene formation commences. Furthermore, the observed activation energy to desorption of the chemisorbed molecule (~ 45 $kJ\ mol^{-1}$) is in good agreement with the theoretical value of 44 $kJ\ mol^{-1}$ calculated for a μ^4 tub-form of COT.¹¹ These observations are consistent with the molecule switching from a flat-lying geometry to a μ^4 configuration, thus accounting for the weak loss at 1420 cm^{-1} (tentatively assigned to a bound $C=C$ mode) as well as the appearance of the previously forbidden $C=C$ and $C-H$ modes at 1680 and 3000 cm^{-1} , respectively. The TPR data do not show any evidence for the formation of benzene from COT at temperatures below ~ 400 K, although this could be due to the large interfering signal from the fragment ion at 78 amu due to COT itself. The HREEL spectra give no evidence for COT \rightarrow benzene conversion at temperatures below ~ 400 K, i.e. below the C_6H_6 desorption temperature; i.e. TPR and HREELS data indicate that this μ^4 species is relatively unreactive toward benzene formation. These data alone do not enable us to determine whether or not benzene reactively formed from COT appears in the gas phase by a process which is surface reaction rate limited or desorption rate limited. The significance of this point is as follows. In the case of ethyne cyclization it is known³ that evolution of benzene into the gas phase is desorption rate limited. Thus if benzene evolution from COT were shown to

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be surface reaction rate limited, this would constitute strong evidence that a pathway involving COT as an intermediate cannot be of major significance in the overall reaction when ethyne is cyclized to benzene on Pd(111).

Large changes in reactive behavior occur when COT is chemisorbed with either NO or C_6D_6 . The surface chemistry is very different in the two cases and these differences are revealing. The TPR data clearly indicate that NO strongly suppresses decomposition of chemisorbed COT; C_6D_6 also strongly suppresses COT decomposition, but in addition it strongly promotes the conversion of COT to benzene. We shall discuss this latter system first.

Cycloreversion of COT to benzene is promoted by coadsorption with C_6D_6 . These results suggest that C_6D_6 may act as a re-orienting agent, inducing a reactive COT chemisorption geometry. The common losses at ~ 700 , 1650, and 3000 cm^{-1} suggest this COT conformation is similar to that formed by high COT coverages alone on Pd(111), i.e. a μ^4 species. Our TPR data show this promotion effect is more pronounced (by a factor of about 2) when the C_6D_6 is chemisorbed first. Earlier work¹⁵ on coadsorption of benzene with NO on Pd(111) showed that preadsorbing the hydrocarbon rendered it relatively immune to subsequent perturbation by NO. This suggests that in the present case C_6D_6 is much more effective in imposing an altered chemisorption geometry on COT when adsorbed first. Further, the appearance of reactively-formed benzene at $<200\text{ K}$ (appearance of 940-cm^{-1} loss (C–C stretch) and associated C_6H_6 desorption) implies that this μ^4 COT species is reactive under conditions similar to those encountered during the ethyne \rightarrow benzene conversion: in particular, it is more reactive than the dominant μ^4 species formed by chemisorption of COT alone. By analogy with ethyne cyclization and benzene chemisorption studies on Pd(111),^{3,25} we assign the low- and high-temperature C_6H_6 desorptions in the present case to tilted and planar benzene molecules, respectively. The coverage dependence of these COT-derived desorption features, strongly bound C_6H_6 favored at low surface coverages, switching to weakly bound C_6H_6 with increased surface crowding, reinforces this view. Conversely, pre-adsorbed COT induces formation of tilted benzene molecules which are associated with high overlayer density. Our previous work^{3,13} on the ethyne \rightarrow benzene system showed that at high coverages all reactively-formed benzene is produced with a tilted geometry.

The similarities between the desorption kinetics of COT-derived C_6H_6 and chemisorbed C_6D_6 in the coadsorbed system show that the appearance of C_6H_6 in the gas phase is a desorption rate limited process. As noted above, this reactive behavior is associated with a μ^4 COT species which is distinct from the unreactive μ^4 that dominates pure COT adlayers. The stable chair conformation of COT (Figure 11) is a plausible chemisorption geometry for the reactive μ^4 species. This is in line with the view adopted by Hostetler et al. for Pt(111)/COT.⁹ Furthermore, as shown below, this hypothesis is in good accord with the expected effects of metal-mediated charge transfer to COT from coadsorbed C_6D_6 .

When COT is pre-adsorbed, the effect on subsequently chemisorbed NO molecules is very striking. On clean Pd(111), NO adsorbs preferentially into 2-fold bridge sites (1550 cm^{-1}), after which atop sites are populated (1720 cm^{-1}). In the presence of COT, adsorption of NO into the atop sites is strongly suppressed, even for saturation doses of NO, while adsorption into the bridge sites still occurs. This implies that a mixed layer is formed (consistent with LEED) and suggests that COT

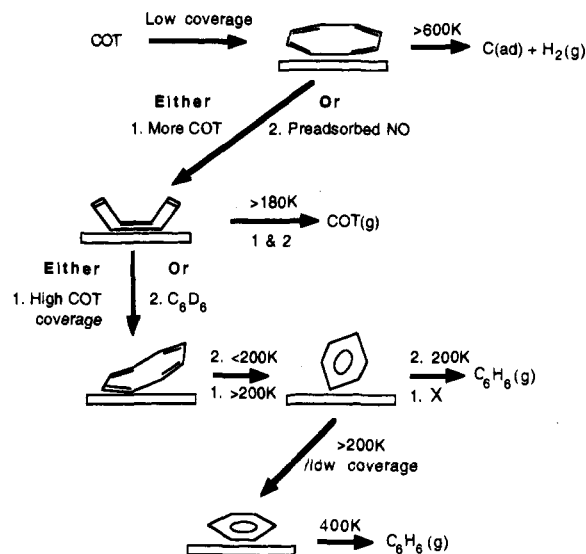


Figure 11. Proposed mechanism of COT transformations on Pd(111), illustrating the influence of NO and C_6D_6 co-adsorbates

molecules preferentially chemisorb atop (site-blocking effect), or that COT electronically disfavors NO adsorption into atop sites. The TPD and HREELS results favor the second explanation: pre-adsorbed COT enhances the binding of NO to the Pd surface, evidenced by weakening of the N–O stretch and the gradual shift to higher temperatures of all NO desorption states. This is discussed further below.

When the chemisorption sequence is reversed (NO first, then COT), as expected, the effects on the reactivity of COT are more pronounced. Decomposition of the molecule is suppressed, while *no reactively-formed benzene is observed*, in marked contrast with the behavior of the μ^4 species that is formed when COT is coadsorbed with C_6D_6 . These results imply that in the presence of pre-adsorbed NO, COT molecules adopt a nonplanar, unreactive geometry. We propose this is the tub-like, μ^4 boat conformation of COT, observed on Pt(111). The $c(4 \times 2)$ and (2×2) LEED patterns observed with increasing NO pre-coverage demonstrate the existence of ordered NO islands, presumably co-existing with islands of COT. As anticipated the observed effects are quite distinct from the mixed layer $C_6D_6 + COT$ system, where neighboring C_6D_6 molecules may perturb the COT. Island formation is also consistent with the negligible influence of COT upon pre-adsorbed NO molecules, in contrast with the strong perturbation of pre-adsorbed C_6D_6 by COT.

It is possible to devise a consistent explanation for all the structural and reactive behavior of COT in the presence of C_6D_6 and NO. In order to do so, we first draw attention to the work of Richards *et al.*²⁶ on mononuclear cobalt complexes of COT. For the neutral molecule, the equilibrium constant for conversion between tub and chair forms of the molecule is <1 . However, when electron transfer to COT takes place, the chair form becomes energetically strongly favored with respect to the boat form ($K > 2 \times 10^5$). Therefore we may argue as follows. Both C_6D_6 and NO are effective in suppressing decomposition of coadsorbed COT simply by occupying vacant metal sites which would otherwise be available for C–H bond dissociation, ultimately leading to fragmentation of the adsorbed hydrocarbon. However, benzene is a strongly electron donating adsorbate so that surface-mediated electron transfer to coadsorbed COT induces μ^4 chemisorption of the chair form—which is the precursor for the cycloreversion reaction. Note that such a dynamic equilibrium is unlikely to exist between the various

(25) Ramirez Cuesta, A.; Valladares, D.; Velasco, A.; Zgrablich, G.; Tysøe, W. T.; Ormerod, R. M.; Lambert, R. M. *J. Phys. Condens. Matter* 1993, 5, A239.

(26) Richards, T. C.; Geiger, W. E. *J. Am. Chem. Soc.* 1994, 116, 2029.

surface-constrained conformers of COT in view of the large barrier to interconversion between such conformers of unbound COT²⁷ (~46 kJ mol⁻¹).

NO is an electron acceptor adsorbed in 2-fold bridge sites and an electron donor²⁰ adsorbed in atop sites. COT, in common with all alkenyl adsorbates, is an electron donor. Co-adsorption of bridging NO with COT should therefore be energetically favored²⁸ and the surface-mediated electron transfer from COT will favor the μ^4 tub form which we therefore identify as the species that is inactive for benzene formation. Correspondingly, adsorption of (electron donor) NO into atop sites should be disfavored in the presence of COT, in agreement with the vibrational and reaction data.

We therefore propose that cycloreversion of COT to benzene proceeds via a two-step mechanism similar to that suggested for COT on Pt(111). However, on Pd(111) a chair μ^4 -COT intermediate appears essential for benzene formation, in contrast with the planar μ^8 -COT species required on Pt; however, in both cases the μ^4 tub form is unreactive toward benzene formation.⁹ Once formed under conditions of high adsorbate density and/or coadsorption of electron donating molecules (such as benzene), the chair μ^4 -COT may undergo ring contraction to bicyclo[4.2.0]octa-1,3,5-triene (BOT) and subsequent retro-cyclization to yield tilted benzene molecules. The ethyne units eliminated during the last step do not desorb directly, nor do they undergo subsequent hydrogenation to ethene, presumably due to the paucity of surface hydrogen available at this temperature (H₂ desorption only at >600 K). Their probable fate is rearrangement to vinylidene at >270 K^{6,29} and decomposition at >400 K eventually forming surface carbon.

Another interesting consequence of the different reaction intermediates formed on Pt and Pd concerns the rate-limiting step for benzene desorption. On Pt(111), product desorption is always reaction rate-limited, irrespective of adsorbate density—a consequence of the high temperature necessary to form planar COT. On Pd(111), and in the absence of coadsorbates, HREELS provides no evidence for the presence of reactively-formed benzene below its desorption temperature. Therefore under these conditions benzene desorption appears to be reaction-rate limited. However in the presence of coadsorbates, reactively-formed benzene appears on Pd(111) below 200 K, implying that evolution of gaseous benzene is a desorption rate-limited process. In the absence of coadsorbates, COT conversion to benzene is lower on Pd(111) than on Pt(111)—35% compared to 50%. This probably results from the threshold COT coverage necessary for reaction on Pd. This coverage threshold is eliminated by C₆D₆ preadsorption, raising COT conversion to around 100%.

From the preceding discussion it is clear that if COT were to be formed under the conditions encountered during ethyne trimerization, it would present an alternative, highly efficient route to benzene. We must therefore consider whether synthesis of a COT intermediate is feasible under these conditions on Pd(111). The failure of previous structural and reaction studies to detect C₈H₈ argues against COT formation from ethyne. However the most probable regime for COT production is that of high adsorbate density, conditions which also favor benzene formation. Under such conditions coadsorption experiments show efficient low-temperature conversion of COT to benzene. Hence observation of a stable COT reaction intermediate is not expected. Furthermore, the intrinsic weakness of COT vibra-

tional features on Pd(111) suggests that small amounts of COT coexisting with C₂, C₄, and C₆ adsorbates would be undetectable. Studies of COT formation from ethyne over Ni catalysts⁸ suggest that the reaction proceeds *via* a C₄H₄ intermediate similar to that involved in acetylene → benzene conversion on Pd(111). However our attempts to induce the same surface reaction between C₄H₄ moieties on Pd(111) were unsuccessful, even at high coverages: neither COT nor benzene desorption were detected. Coadsorption of NO and C₆D₆ with DCB also failed to induce C₄ → C₈ coupling.

Our results indicate that more than one type of chemisorbed COT species can be formed on the Pd(111) surface and only one of these (μ^4 chair form) is active for benzene formation: the flat-lying form undergoes total decomposition, and the tub form is unreactive. We have also demonstrated that it is indeed possible to convert COT to benzene on Pd(111) at relatively low temperatures. Hence we cannot absolutely rule out eq 2 as a possible reaction pathway: benzene formation from C₈H₈ formed as a surface intermediate by the coupling of two C₄H₄ metallacycles. Nevertheless, all attempts to produce COT and/or benzene from C₄H₄ under conditions of temperature and total coverage appropriate to ethyne cyclization were unsuccessful, suggesting that under cyclization conditions, at best only a very small fraction of ethyne reacts to form COT over Pd(111). Thus we conclude that eq 2 cannot be a major pathway in the coupling of ethyne to form benzene on Pd(111) and that the dominant pathway is that represented in eq 1.

Conclusions

1. Cyclooctatetraene is reactive toward benzene formation on Pd(111). At low coverages COT adopts a μ^8 conformation which undergoes decomposition to carbon. Higher COT coverages result in formation of an unreactive, weakly bound, μ^4 tub form of COT, akin to that observed on Pt(111). Above a critical threshold COT coverage reaction to benzene commences, possibly via a μ^4 chair COT intermediate. Benzene desorption appears reaction-rate limited, and the maximum clean surface conversion is only ~35%.

2. Coadsorption of an electron donor (C₆D₆) which forms a mixed adlayer with COT induces ~100% conversion to benzene. This is consistent with C₆D₆ promoting the chemisorption of COT in a μ^4 chair conformation—the species which results in efficient benzene formation at low temperatures (<200 K). Under these conditions benzene desorption is the rate-limiting step for the appearance of gaseous benzene.

3. NO, an electron-withdrawing adsorbate, stabilizes the unreactive μ^4 tub form of COT relative to the reactive planar μ^8 and μ^4 chair species, decreasing both COT decomposition and reaction to benzene. The surface phase formed by NO and COT coadsorption is critically dependent on the adsorption sequence, a consequence of the similar interaction strengths of NO and COT with Pd(111). Islands of NO and COT are generated when NO is pre-adsorbed, whereas a mixed NO/COT layer results from pre-adsorption of the hydrocarbon.

4. Although COT → benzene can be a facile process, 2C₄H₄ → COT is not. Attempts to induce coupling to yield COT at high coverages were unsuccessful, even in the presence of NO or C₆D₆. Therefore it is unlikely that COT is an intermediate in the principal reaction pathway when ethyne is cyclized on Pd(111).

Acknowledgment. A.F.L. thanks the EPSRC and BP International for sponsorship under CASE Studentship 92562498. C.J.B. acknowledges financial support by the EPSRC who also supported this work under Grant No. GR/J00632.

JA950607T

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