Quantitative Investigation of the Decomposition of Cyclooctene on Pt(111) Using BPTDS

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Other researchers have reported (*J. Am. Chem. Soc.* **1993**, *115*, 2044; *J. Phys. Chem.* **1994**, *98*, 2952) that cyclooctene dehydrogenates on Pt(111) to stable adsorbed cyclooctatetraene, which then undergoes ring contraction to produce benzene but without any calibrated measurements of the yield. Here, quantitative thermal desorption mass spectrometry (TDS) and bismuth postdosing thermal desorption mass spectrometry (BPTDS) are used to investigate the conversion of cyclooctene to benzene on the Pt(111) surface. Our results show that although benzene is formed, it is a very minor product, corresponding to less than 2% of a monolayer (including both adsorbed and gas-phase benzene). Most of the adsorbed cyclooctene either desorbs intact at low temperatures (∼10%) or simply dehydrogenates (∼90%), ultimately to surface carbon by 800 K, but without going through adsorbed benzene as an intermediate. Stable intermediates with stoichiometries C_8H_{12} and C_8H_6 are identified by TDS to be present at 350 and 430−560 K, respectively, but BPTDS shows that neither of these correspond to a simple molecularly adsorbed state of a stable gaseous molecule. During the conversion between these two species, however, cyclooctatetraene is produced transiently at 430 K, suggesting that both of these species still have an intact C_8 ring.

Introduction

Catalytic reactions of hydrocarbons are perhaps the largest class of reactions used in industrial chemistry, but the mechanisms of the reactions are often unknown. In an attempt to understand the fundamental chemistry of hydrocarbon catalysis, single-crystal substrates in ultrahigh-vacuum systems are commonly used to model reactions under carefully controlled conditions.

Accurately quantifying the reaction products in such experiments can be difficult but is of utmost importance in order to decide which of many possible chemical pathways are dominant. Quantitative thermal desorption mass spectrometry (TDS) is typically used to determine product distributions by analyzing the molecules or fragments that desorb during a heating cycle, but it is of limited utility because not all products may desorb intact. Furthermore, some surface species, benzene in particular,[1] will not desorb at all if they are present in only small coverages, as is the case for many surface reactions in UHV.

In situations such as these, bismuth postdosing thermal desorption mass spectrometry (BPTDS) has been shown to be an effective tool for identifying and quantifying adsorbed molecules.[2] It has been found that by coadsorbing a monolayer of bismuth with molecularly adsorbed hydrocarbons, the hydrocarbons will quantitatively desorb at low temperatures (150−300 K). The effect of the bismuth is 2-fold. First, Bi passivates the hydrocarbon adlayer, preventing additional bond breakage within most surface species. Second, Bi weakens adsorbate−substrate bonds, to the point that quantitative desorption of molecules that have a stable gas-phase analogue is possible. These characteristics allow one to use BPTDS to get a *quantitative* measure of some of the species present on a surface during an experiment.

In this work, BPTDS has been used to investigate the mechanism of decomposition of cyclooctene (COE) on a Pt(111) surface. Other researchers[3,4] have suggested that benzene, formed via a stable bicyclic cyclooctatetraene surface intermediate, is the dominant product in COE decomposition, but their data allowed only qualitative conclusions. Adsorbed benzene is easily quantified by BPTDS on Pt(111).[2] The results of BPTDS experiments presented here indicate that benzene is only a minor product, and cyclooctatetraene is produced only transiently on the surface. Additionally, stoichiometric analysis of the H_2 signal from TDS experiments with COE on Pt(111) indicates that there are stable intermediates of C_8H_{12} and C_8H_6 stoichiometry. A mechanism is proposed for COE decomposition (see Figure 1), which is also consistent with prior results.[3,4]

Experimental Section

All of the experiments described here were performed in an ultrahigh-vacuum chamber that has been described previously.[5] In these experiments, however, the mass spectrometer was operated without an aluminum focusing cone that had been used previously to eliminate any signal from the back or sides of the sample, because the surface of this cone was found to catalyze the formation of benzene.

The Pt(111) crystal used in these experiments was cleaned by sputtering with 2.6 kV Ar^+ ions at a sample current of 25 μA for 3 min while heating to 1100 K and then annealing at 1100 K for 3 min. Benzene and cyclooctene were dosed directly to the sample using an apparatus described previously.[6] The experimental procedures for TDS and BPTDS have also been described in detail elsewhere.[2,5] Briefly, BPTDS experiments were performed by dosing COE to the surface at 100 K, heating the surface to the desired temperature (the "flash temperature"), and immediately cooling back to 100 K, dosing about 1 ML of Bi from an effusive metal source, and then tracking up to six masses at a time on a multichannel quadrupole mass spectrometer while heating the sample, as in a standard thermal desorption experiment.

The benzene and COE used in these experiments were obtained from Aldrich. The benzene was 99+% pure, and the COE was 95% pure, with the remainder cyclooctane. Each of these was degassed with several freeze−pump−thaw cycles just prior to dosing, and their purity was verified in situ with mass spectrometry.

Our measured cracking pattern for COE agreed with the literature[7] when corrected for the transmission function of our

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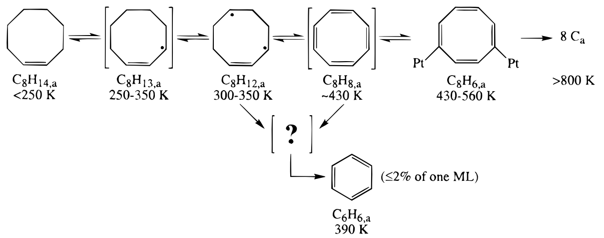

Figure 1. Mechanism for the decomposition of cyclooctene on the Pt(111) surface, proposed on the basis of present results and those in refs 3 and 4. Species in brackets do not necessarily correspond to stable stoichiometries and may exist only transiently. The double bonds and radical electrons shown in the species here are not intended to imply actual electronic structure and might represent σ-bonds to the Pt surface. They are intended only to specify the number of hydrogens remaining on each species. While the stoichiometries of the $C_8H_{12,a}$ and $C_8H_{6,a}$ species are quite clear, the geometries suggested here are very tentatively proposed.

mass spectrometer, which decays rapidly with mass. The transmission function had been estimated previously[8] by comparing the observed cracking patterns of several pure hydrocarbons with their published cracking patterns, taken from reference 7. It was shown to decrease as $e^{-0.04m/z}$ relative to the transmission function of instruments used to record the spectra compiled in reference 7. (Such instruments typically have a relatively constant transmission, at least in the mass range of interest (m/z < 120).)

The BPTDS peaks in our measured mass spectra were sometimes composed of COE, cyclooctadiene (COD), cyclooctatetraene (COT), or benzene, or a mixture thereof. The relative abundances of these four species in such peaks was estimated in the following way. The time-integrated mass intensities for such a BPTDS peak, averaged over several experiments, was first divided by the transmission function of our mass spectrometer ($e^{-0.04m/z}$), to mimic the pattern which would have been collected with an instrument of constant transmission. This corrected pattern was then fit to a linear combination of the literature cracking patterns of the four species listed above. To ensure that the coefficients in this fit would reflect the relative partial pressures of each of these four molecules, the literature cracking patterns used in this fit were taken from a standard compilation,[7] but first normalized by dividing by the mass-summed total ion intensity in that molecule's literature cracking pattern and multiplying by the ion gauge sensitivity factor for that molecule (taken from ref 9). The total ion intensity collected for different molecules at a constant pressure by a mass spectrometer of constant transmission should just be proportional to the ion gauge sensitivity factor for that molecule. Therefore, normalizing the literature cracking patterns in this way is like using cracking patterns for different molecules that were collected at the same pressure for each molecule. (The conclusions of this paper are insensitive to even 3-fold errors in this correction method, which is certainly more accurate than that for the mass range (m/z = 25−120) and species studied here.)

All measurements of cyclooctene desorption reported in this paper were performed with slightly more than 1 monolayer (ML) of cyclooctene dosed to the surface, unless otherwise stated. (One monolayer is defined here as the coverage which just leads to the onset of a multilayer TDS peak.)

Results

First, slightly more than 1 monolayer of benzene was dosed onto clean Pt(111), as a calibration standard. A representative thermal desorption spectrum of benzene adsorbed on Pt(111) is shown in Figure 2a for $m/z = 2$ and $m/z = 78$. These curves agree with those reported in the literature[1] for the TDS of benzene. In the $m/z = 78$ curve, desorption from the multilayer is seen at about 195 K, and a broad desorption feature is observed between 300 and 600 K, corresponding to desorption of 45% of a monolayer of adsorbed benzene.[1] The $m/z = 2$ curve displays three prominent features (marked A, B, and C) which have been assigned[1] to

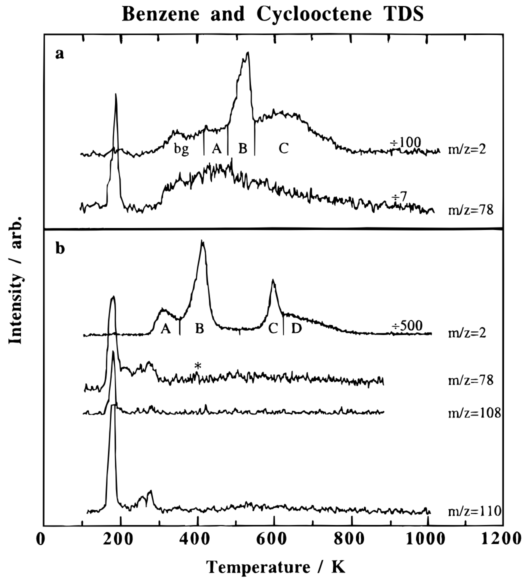

Figure 2. Thermal desorption curves for (a) slightly more than a monolayer of benzene and (b) slightly more than a monolayer of cyclooctene on Pt(111). Except for the scaling factors shown on some curves, the mass spectrometer intensity ranges and multiplier voltages are the same for all curves in both (a) and (b), so intensities can be directly compared. Desorption intensity due to background H_2 adsorption is labeled "bg".

$$C_6H_{6,a} \xrightarrow{420-565\ \mathrm{K}} {}^3/_2H_{2,gas} + C_6H_{3,a}\ (\text{or } 3C_2H_a) \qquad (A+B)$$

$$C_6H_{3,a} \xrightarrow{565-810\ \mathrm{K}} {}^3/_2H_{2,gas} + 6C_a \qquad (C)$$

The area in Figure 2a marked "bg" was shown[1] to be due to background H_2 adsorption. This was confirmed here by control experiments in which only the background peak due to H_2 was allowed to build up, without dosing benzene to the surface. The verticle cutoff shown here represents a crude separation of this feature's proper size and shape from the additional features that appeared whenever benzene was leaked into the chamber and the sample was rotated into its directed doser.

Next, cyclooctene was dosed to clean Pt(111). A representative TDS of cyclooctene is presented in Figure 2b for $m/z = 2$, 78, 108, and 110. For $m/z = 78$, 108, and 110, COE exhibits peaks at about 180 and 270 K, corresponding to desorption from the multilayer and monolayer, respectively. In addition, the $m/z = 78$ spectrum shows a small but reproducible peak (marked with an asterisk) at about 390 K that also has been reported by others,[4] but with far better signal-to-noise than is shown here, due to instrumentation differences. They have attributed this peak to desorption of benzene formed via cyclooctene ring contraction. Note, however, by comparison of the $m/z = 78$ curves in Figure 2, that the amount of benzene desorption following COE adsorption is much, much less than that seen following benzene adsorption.

The H_2 TDS in Figure 2b shows four distinct features at 295, 400, 600, and 620−770 K (broad), marked A−D, respectively. The ratios of the integrated areas under the H_2 TDS curve are A:B:(C+D) = (1.99 ± 0.06):(6.04 ± 0.15):(5.97 ± 0.10), which indicates the following stoichiometry for the dehydro-

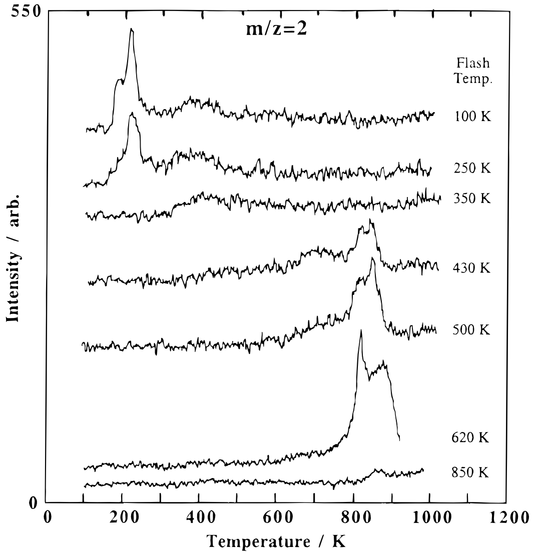

Figure 3. BPTDS intensity for *m*/*z* = 2 after flashing the surface dosed with ~1 ML of COE to the indicated temperatures. This mass tracks H_2. Intensity range = 10^{-9} A. The peaks near 200 K in the top two curves are just part of the cracking pattern of COE.

genation of COE:

$$C_8H_{14,a} \xrightarrow{270-360\ K} H_{2,g} + C_8H_{12,a} \qquad (A)$$

$$C_8H_{12,a} \xrightarrow{360-430\ K} 3H_{2,g} + C_8H_{6,a} \qquad (B)$$

$$C_8H_{6,a} \xrightarrow{560-770\ K} 3H_{2,g} + 8C_a \qquad (C+D)$$

These represent net stoichiometries, which could, in principle, be achieved by combining fragments with fewer than eight carbon atoms. It will be argued below, however, that the C_8 ring probably stays intact up to above 430 K.

The absolute amount of COE which dehydrogenates on Pt(111) can be estimated by comparing the integrated intensity of the H_2 TDS spectrum from a saturated monolayer of COE with that from a monolayer of benzene adsorbed on Pt(111). Benzene has a surface density of 0.16 ± 0.012 molecules/Pt atom, or 2.4×10^{14} molecules/cm^2, of which 55% (or 1.3×10^{14} molecules/cm^2) dehydrogenate to give three H_2 molecules per benzene.[1] It was observed that COE produces 3.5 times as much H_2 as is produced by a monolayer of benzene. Accounting for the difference in production of H_2 when COE and benzene dehydrogenate (each benzene molecule produces three H_2 molecules, while each COE molecule produces seven H_2 molecules), this indicates that about 1.5 times as many COE molecules as benzene molecules dehydrogenate during TDS. This translates into a surface density of 2.0×10^{14} COE molecules/cm^2 that dehydrogenate. It will be shown below that 90% of a COE monolayer dehydrogenates, so this sets the monolayer coverage of COE on Pt(111) at about 2.2×10^{14} molecules/cm^2.

To help identify the adsorbed intermediates produced upon heating during the TDS of COE, BPTDS analysis was performed on surfaces that had been dosed with about 1 monolayer of COE and flashed to a predetermined temperature. Representative BPTDS curves are presented in Figures 3−7 for *m*/*z* = 2, 78, 93, 104, and 110, respectively. In these experiments, *m*/*z* = 2 follows H_2; *m*/*z* = 78 follows benzene, COD, and COT; *m*/*z* = 93 follows COD (with a very low contribution from COE); *m*/*z* = 104 follows COT; and *m*/*z* = 110 follows COE. Other masses were also followed (*m*/*z* = 26, 39, 52, 67, 95, 106, 108, and 112), although only six masses at a time could be monitored

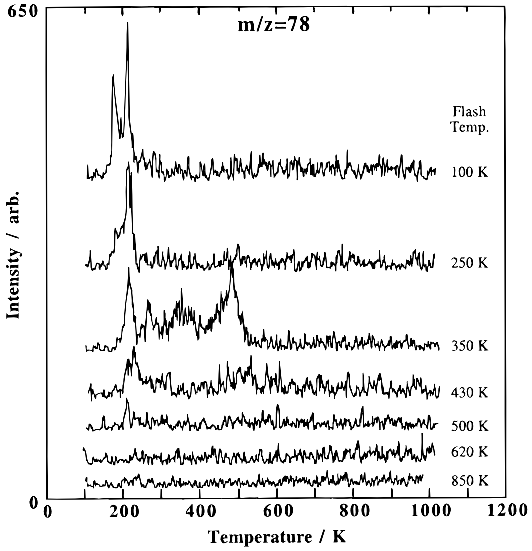

Figure 4. BPTDS intensity for *m*/*z* = 78, as in Figure 3. This mass tracks cyclooctadiene, cyclooctatetraene, and benzene. One monolayer of molecularly adsorbed benzene produces a BPTDS peak for this mass at 190 K, which is about 20 times more intense than the 100 K spectrum of COE shown here. Intensity range = 10^{-11} A.

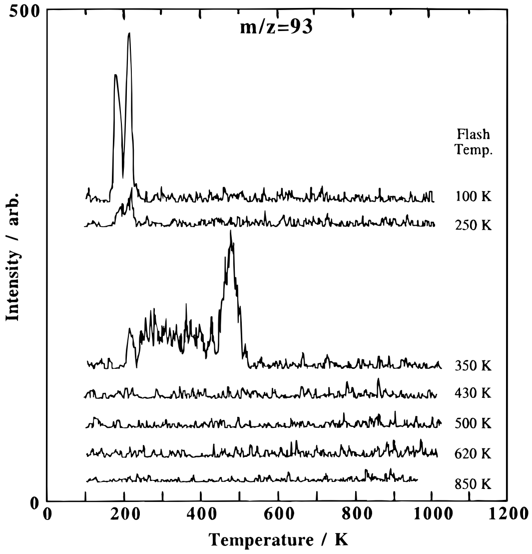

Figure 5. BPTDS intensity for *m*/*z* = 93, as in Figure 3. This mass tracks cyclooctadiene, with a small (~2%) contribution from cyclooctene. Intensity range = 10^{-11} A.

in any one spectrum. The mass spectra in Figure 6 are only shown below 650 K because of a high-temperature feature at this mass and others, shown by control experiments to correspond to the background desorption of hydrocarbons from the sample holder and chamber walls, which was unimportant to the surface chemistry on Pt(111). (These control experiments were performed by repeating exactly the same experiments, except without rotating the sample into the directed doser when introducing COE.)

For flash temperatures of 100 K (i.e., no flash) and 250 K, COE desorbs from the surface in two BPTDS peaks at 190 and 210 K. The intensity of the peak at 190 K decreases with increasing flash temperature faster than the peak at 210 K, but it is not possible to completely remove the former peak without also removing much of the latter. No significant products besides COE were observed at these flash temperatures in the BPTDS experiments. The amount of COE which desorbs in BPTDS with no flash is about 10 times greater than that which desorbs as COE from the same dose in normal TDS. This proves that about 90% of a monolayer of COE dissociates in

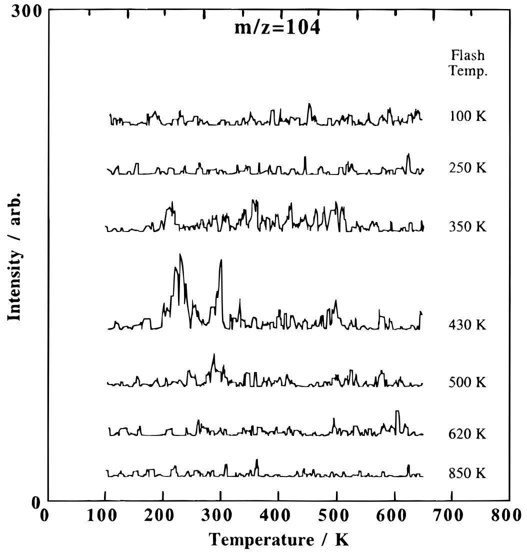

Figure 6. BPTDS intensity for *m/z* = 104, as in Figure 3. Note the different temperature axis. This mass tracks cyclooctatetraene. Intensity range = 10^{-11} A.

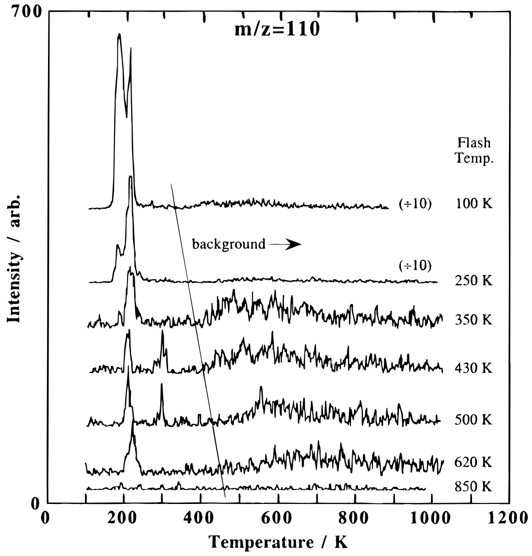

Figure 7. BPTDS intensity for *m/z* = 110, as in Figure 3. This mass tracks cyclooctene. The intensity above the slanted vertical line is attributed to background due to outgassing from the sample holder, which is removed during the higher-temperature flashes. Intensity range = 10^{-11} A.

normal TDS, since the COE desorbs quantitatively in BPTDS (as do all other adsorbed molecules ever probed by BPTDS on Pt(111)[2]).

By a flash temperature of 350 K, COE starts to dehydrogenate and decompose, as seen in the BPTDS desorption of Figures 3−7. Analysis of the results from the 350 K flash experiment shows that the products desorbing consist of approximately 60% COE, 25% COD, 5% COT, and 10% benzene. If the readsorption of background COE after the initial flash is taken into account (see below), this product distribution shifts to approximately 50% COE, 35% COD, 5% COT, and 10% benzene. While the percentage of desorption products other than COE increases with increasing flash temperature, the absolute amount of desorption products decreases by a factor of 20 between the 250 and 350 K flashes (and by another factor of 5 by the 430 K flash).

After flash temperatures of 430 K and above, a high-temperature H_2 BPTDS peak is seen above 800 K. The temperature of about 850 K from this peak is coincident with the onset of Bi desorption from the Pt(111) surface,[2,10] so it seems likely that this H_2 evolution corresponds to dehydrogenation of adsorbed hydrocarbon fragments as Bi desorption produces vacant sites on the surface. Previously, similar peaks have been interpreted in this way.[2,11]

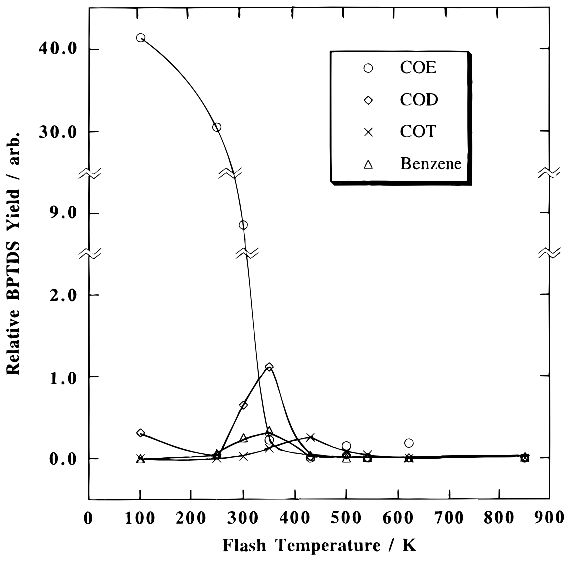

Figure 8. Distribution of products formed during the thermal decomposition of cyclooctene on Pt(111), determined by BPTDS measurements. The relative intensity of cyclooctene has been corrected for background readsorption, as described in the text.

For a 620 K flash temperature, only COE is observed in the desorbing products. Since all significant amounts of COE should have been removed from the surface at temperatures much lower than this, the observed COE must be due to readsorption from the background as the sample is cooling back to 100 K after the flash. Varying the time that the vacuum chamber is allowed to pump down between initially dosing COE to the surface and flashing the sample to 620 K confirms this; the amount of COE desorbing in BPTDS decreases with a longer pumping time. The 620 K curve presented in Figure 7 is typical of those recorded for the 7 min delay between dose and flash that was used in this experiment and was used to correct the lower flash temperature BPTDS curves for COE readsorption.

The absence of significant BPTDS desorption products (except for a much smaller high-temperature H_2 peak) after the flash to 850 K suggests that dehydrogenation is nearly complete at this temperature. This is consistent with results for numerous other hydrocarbons on Pt(111), where complete dehydrogenation to graphitic carbon occurs by 850 K.[1,11]

A summary of the distribution of the products of COE decomposition, determined from BPTDS measurements, is presented in Figure 8. The products that were clearly identified were COE, COD, COT, benzene, and H_2. The relative yields of these species depended upon the flash temperature, as shown in Figure 8. The yields were determined by first averaging the results from numerous BPTDS experiments at the same flash temperature to obtain the average distribution of integrated mass intensities for each BPTDS peak. These were then fit to the pressure-normalized cracking patterns of the molecules listed above, determined as described in the Experimental Section. In addition to these products, a small amount of unexplained intensity was observed at flash temperatures above 350 K for *m/z* = 26, 39, and 52. These are typical masses for many hydrocarbons, and it has not been possible to assign this intensity to a particular parent molecule. Styrene and ethylbenzene, two likely candidates, were ruled out as the sources of the extra intensity at the masses listed.

Each of the data points in Figure 8 represents the total amount of a given molecule that desorbed during BPTDS after a flash to the indicated temperature. Many of the data points combine yields of the products from more than one BPTDS peak, and a detailed description of the desorption temperatures of each product is included below.

The initial large BPTDS intensity of COE for the 100 K and 250 K flash temperatures in Figure 8 appears in two low-temperature states (about 190 and 210 K) in the BPTDS experiment (see Figure 7). Such low BPTDS temperatures typically correspond to a simple molecular adsorption state for the hydrocarbon.[2] As shown in Figure 8, the amount of this molecularly adsorbed COE decreases nearly to zero by a flash temperature of 350 K.

It is likely that the tiny amount of COD shown in Figure 8 after a 100 K flash (i.e., as dosed, with no flash before Bi postdosing) is actually an artifact of noise in the cracking pattern of COE. Otherwise, COD is observed only desorbing in significant quantities in the BPTDS experiments after flashes to 300 and 350 K. For both of these flash temperatures, about 20% of the COD intensity desorbs at about 210 K in BPTDS, while the other 80% desorbs in a 470 K BPTDS peak (see Figure 5).

No significant COT desorbs during BPTDS except for flash temperatures near 430 K in Figure 8, and here the BPTDS intensity is at 220−300 K (see Figure 6). Again, this low BPTDS temperature suggests that a small amount of molecularly adsorbed COT is produced by flashing to 430 K (see Figure 4).

Finally, significant benzene desorption in BPTDS is observed only after flashes to 250−350 K (see Figure 8). For the 250 K flash, the benzene desorbs at about 210 K in BPTDS, while most of the benzene that desorbs after the 300 and 350 K flashes is in a 470 K BPTDS peak.

Discussion

An investigation of the temperatures at which the products shown in Figure 8 desorb in the BPTDS experiments is helpful in determining the details of the mechanism for cyclooctene dehydrogenation. In general, desorption at low temperatures (≤300 K) in BPTDS experiments indicates that the desorbing molecule was actually present on the surface in molecular form before bismuth dosing or heating began.[2] In these cases, BPTDS has always proven to be nearly quantitative in its desorption of the molecular adsorbate,[2] as is also the case for molecularly adsorbed benzene on Pt(111).[2,5] Higher temperature desorption, however, typically indicates that the surface species present at the beginning of BPTDS heating had to undergo additional reaction, such as gaining or losing a hydrogen, before desorption as a stable gas-phase molecule was possible.[2] The interpretation of BPTDS peaks above 300 K is therefore somewhat ambiguous. When coadsorbed H adatoms are also present, BPTDS peaks below 300 K can be due to the hydrogenation of molecular fragments that lack one H atom from having a stable gas-phase analogue.[2] Since H adatoms are nearly quantitatively removed from Pt(111) by flash temperatures of 380 K and above, this possibility need be considered only when interpreting BPTDS results for flash temperatures *below* 380 K.

BPTDS analysis, combined with the stoichiometry determined above from normal TDS, allows likely intermediate species in the decomposition of cyclooctene to be inferred from the data. As shown above, about 90% of the initial COE monolayer decomposes during TDS. The BPTDS signals shown in Figure 8 for COD and COT are far too small to be attributed to quantitative conversion of this 0.9 ML of COE to adsorbed COD or COT during the original flashes. The high BPTDS temperature at which most of the COD is observed suggests that this signal does not originate from a *molecular* adsorbate formed prior to BPTDS. However, the stoichiometry from the H_2 TDS in Figure 2b indicated a stable C_8H_{12} species near 360 K. In addition, a stable C_8H_6 intermediate exists between 430 and 560 K. Possible identities of these intermediates can be suggested from the results of some of the BPTDS experiments.

First, the low yields of COD and COT identified in both BPTDS and, previously, in TDS,[4] after heating the surface to above 350 and 430 K, respectively, suggests that the C_8 ring is still intact up to at least 430 K.

The high-temperature BPTDS desorption state that occurs for COD after a flash to 350 K might result from the presence of an allylic C_8H_{13} species at this temperature, which would be required to give up a single hydrogen before desorbing in BPTDS as COD. Allylic intermediates are commonly seen from 250−350 K on Pt(111) during the decomposition of alkenes,[5,12] lending credence to this hypothesis. (When such allyl species are coadsorbed with hydrogen adatoms, they hydrogenate readily during BPTDS at about 200 K to produce the starting alkene.[2,5,12] Thus, the conversion to this allyl may have started already at about 250 K and given rise to some of the COE signal seen at this flash temperature, where coadsorbed H may also be present in large quantities.)

Since adsorbed dienes have been proven to desorb quantitatively in BPTDS,[2] the low BPTDS yield of COD at any flash temperature suggests that this diene never actually exists in large concentrations during the decomposition of COE. Thus, the adsorbed species with C_8H_{12} stoichiometry, determined from the H_2 TDS curve in Figure 2b to exist at 360 K, is not likely to simply be the species that would be produced by the molecular adsorption of COD. Instead, a species such as that pictured in Figure 1 is tentatively postulated, where the second H atom is abstracted from the γ-carbon. A simple ball-and-stick model of the allylic species indicates that it could adopt a symmetrical surface geometry where the indicated γ-H would be most easily abstracted in the next dehydrogenation step. This species would also be expected to desorb as COD at relatively high BPTDS temperatures, and only with low yield, since sequential C−H bond cleavage and formation would be necessary.

The lack of any significant desorbing products for flash temperatures greater than 430 K (Figure 8), combined with the absence of decomposition observed between 430 and 560 K in the H_2 trace during thermal desorption of COE (Figure 2), indicates a fairly stable, strongly bound molecular fragment present from 430 to 560 K. An intermediate species with an intact C_8 ring and two additional σ-bonds to the surface is tentatively proposed to explain these observations, as well as the C_8H_6 stoichiometry indicated by TDS (see Figure 1). The η^8-C_8H_8 intermediate, proposed to exist at 472 K by Hostetler et al.[3,4] based on HREELS spectra in their investigation of the dehydrogenation of cyclic C_8 alkenes, clearly has the *in*correct stoichiometry. One could argue that the C_8H_6 stoichiometry indicated by TDS here is really due to a combination of several species, for example, a 50:50 mixture of C_8H_8 and C_8H_4 species. However, the fact that this surface structure is stable over such a broad temperature range (from 430 to 560 K) suggests a single species. Also, the combination of two such species would give rise to many more peaks in the HREELS spectra and still would require complete reinterpretation of the spectra. The simplest explanation, which is the one we prefer, is that a single species of C_8H_6 stoichiometry dominates the surface at these temperatures. Indeed, the HREELS spectra obtained by Hostetler et al. after the adsorption of either 1,3-COD, 1,5-COD, or COT (all of which they showed produce the same intermediate as COE in this temperature range[4]) appear to be consistent with the alternative C_8H_6 intermediate tentatively proposed here.

Surface geometry seems favorable for the proposed C_8H_6 intermediate: the third-nearest-neighbor distance on the Pt(111) surface is 5.54 Å, approximately what might be expected for the distance between two Pt atoms σ-bonded to carbon atoms in the 1- and 4-positions on the COT ring. (The distance between the H atoms in these two positions is about 5.3 Å.) The presence of two additional Pt−C σ-bonds also could explain the species' resistance to removal by side reactions in BPTDS.

Incorporating all of these implications, a proposed mechanism for the decomposition of COE on Pt(111) is shown in Figure 1. Molecular COE is the only hydrocarbon species we ever observed with BPTDS in large quantities after dosing COE, either before or after annealing it. The large magnitude of the COE BPTDS signal after annealing to 250 K or less reveals that it is still mostly molecularly adsorbed. Between 250 and 350 K, it loses an allylic hydrogen to form a species that cannot be desorbed directly with BPTDS. By 350 K this allyl adsorbate loses another hydrogen at the γ-carbon, yielding a C_8H_{12} species which again cannot be directly desorbed in BPTDS. This species begins to dehydrogenate at ∼360 K. It may transiently convert to an adsorbed COT species, as suggested by the low yield of COT in both TDS at 440 K[4] and in BPTDS after the 430 K flash. This must quickly dehydrogenate further to form the C_8H_6 intermediate pictured in Figure 1, with two extra Pt−C σ-bonds stabilizing the adsorbate. This species remains stable from ∼440 to 560 K. Heating it above 560 K causes it to dehydrogenate further. Dehydrogenation is complete by 850 K, at which point only graphitic carbon remains on the surface.

The high temperature of the BPTDS peaks for benzene indicates that it probably is produced during BPTDS by reaction of some unobserved surface species. The small amount of benzene observed in both TDS and BPTDS supports the assumption that the reaction pathway that produces benzene is only a minor side reaction, as shown in Figure 1. The most intense TDS peak for benzene occurs at about 390 K, suggesting that it is produced during the conversion from the C_8H_{12} to the C_8H_6 species.

The amount of benzene formed by decomposition of COE can be quantified with TDS by comparing the area of the $m/z = 78$ curve obtained when a monolayer of benzene is dosed directly to a Pt(111) surface (Figure 2a) with the area of the $m/z = 78$ curve from the COE TDS experiment (Figure 2b). Assuming that all of the intensity in the $m/z = 78$ curve in the COE TDS arises from benzene, the area of this curve (above 350 K) is only 1.7% of the area of the $m/z = 78$ trace (above 230 K) in the benzene TDS. Only 45% of the molecules in a monolayer of benzene adsorbed on Pt(111) will desorb in a TDS experiment (the other 55% dehydrogenate to leave surface carbon).[1] When this factor is taken into account, the benzene that desorbs during a COE TDS experiment corresponds to only 0.8% of a monolayer of benzene.

For comparison, the amount of adsorbed benzene formed during the COE TDS experiment can be measured with BPTDS[2] and related to the BPTDS signal from a monolayer of benzene dosed directly to a Pt(111) surface. The BPTDS peak area of the $m/z = 78$ signal after a 350 K flash (which gave the largest $m/z = 78$ signal in the COE BPTDS experiment) is compared with the BPTDS peak area of the $m/z = 78$ signal from a monolayer of adsorbed benzene at 100 K. This comparison indicates that decomposition of COE on Pt(111) yields <1.1% of a monolayer of adsorbed benzene. (In this comparison, it is useful to remember that adsorbed benzene at 100 K is quantitatively desorbed as molecular benzene in BPTDS, even after it has been preflashed to 380 K.[2,5])

In both of the previous calculations, it was assumed that the $m/z = 78$ signal in the COE decomposition experiments consisted solely of benzene. However, $m/z = 78$ also tracks desorption of COD and COT, and the former is produced in significant amounts over the same temperature range as benzene in BPTDS, so the calculated yields of benzene from COE surface decomposition clearly must be taken only as upper limits. Given these considerations, the total amount of benzene produced by decomposition of COE is less than 2% of a monolayer.

Comparing the H_2 TDS curves from COE with that from benzene in Figure 2 further suggests that the total amount of benzene produced by decomposition of COE is small. The H_2 TDS peaks from cyclooctene above 300 K *in no way* resemble those characteristic of benzene dehydrogenation, whether the benzene is directly adsorbed, as in Figure 2a, or produced by dehydrogenation of larger hydrocarbons.[13,14] The complete dissimilarity of the hydrogen evolution from the two molecules, especially the conspicuous absence of the characteristic H_2 TDS for benzene at about 500 K,[1] indicates that if any adsorbed benzene is produced, it is present in very low quantities.

Conclusion

Using BPTDS and quantitative TDS, it has been shown that when a monolayer of cyclooctene is dosed to Pt(111), about 10% of the original cyclooctene monolayer desorbs below 350 K, and the remainder undergoes successive dehydrogenation to produce graphitic carbon. COE is converted to benzene with less than 2% yield. In the dehydrogenation of COE, a species of stoichiometry C_8H_{12} is stable at 350 K. Between 430 and 560 K, an adsorbed intermediate species with stoichiometry C_8H_6 (determined by TDS) is present. Neither of these species gives significant low-temperature BPTDS yields, indicating that they are not composed of molecularly adsorbed versions of stable gaseous molecules. Low yields of COT in both TDS and BPTDS suggest that adsorbed COT may be a transient intermediate at 430 K in the conversion of the C_8H_{12} species to the C_8H_6 species. Above 560 K, the C_8H_6 intermediate simply decomposes to yield hydrogen gas and surface carbon by 850 K.

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