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# Iodobenzene on Pd(111) studied by thermal desorption spectroscopy and laser-induced thermal desorption–Fourier transform mass spectrometry

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## Abstract

Iodobenzene decomposes on Pd(111) and forms benzene, iodine, adsorbed carbon, and hydrogen. At low initial iodobenzene exposures no iodobenzene desorbs, benzene desorbs at 500 K, and hydrogen desorbs between 500 and 700 K, indicative of decomposition of some of the benzene. At high initial exposures iodobenzene desorbs at about 200 K and benzene desorbs at about 160 K; however, no hydrogen desorbs. Iodine desorbs from Pd(111) around 1000 K. Adsorbed iodine atoms passivate the Pd(111) surface toward the decomposition of iodobenzene and the dehydrogenation of benzene. Experiments with perdeuterated iodobenzene show that the benzene forms from reaction of phenyl with sub-surface hydrogen by 143 K. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Iodobenzene; Laser-induced thermal desorption (LITD); Pd(111); Phenyl iodide; Thermal desorption spectroscopy

## 1. Introduction

The study of alkyl fragments on metal surfaces has important application, since alkyl groups are frequently postulated as intermediates in catalytic reactions [1]. Understanding how these hydrocarbon species react on surfaces can provide information on various processes. Alkyl iodides are useful compounds for producing alkyl groups on metal surfaces, because the carbon–iodine bond can be thermally activated at low temperatures [1]. Few surface science studies have characterized alkyl iodide reactions on palladium, in particular the chemistry of phenyl groups on Pd(111). Solymosi and co-workers [2–5] have studied the

CH<sub>3</sub>, CH<sub>2</sub>, and CH<sub>3</sub>CH<sub>2</sub> species on Pd(100), formed from CH<sub>3</sub>I, CH<sub>2</sub>I<sub>2</sub>, and CH<sub>3</sub>CH<sub>2</sub>I, respectively. They found that CH<sub>3</sub> hydrogenates to methane, CH<sub>2</sub> hydrogenates to methane and dimerizes to form ethene, and CH<sub>3</sub>CH<sub>2</sub> both hydrogenates to ethane and dehydrogenates to ethene. On Pd(111) only the chemistry of CH<sub>3</sub>I has been studied by Chen and Winograd [6]. Whereas CH<sub>3</sub>I adsorbs dissociatively on Pd(100) [2], CH<sub>3</sub>I adsorbs molecularly on Pd(111) then decomposes to adsorbed CH<sub>3</sub>, which then hydrogenates to methane [6]. The rate-limiting step of the reaction of methyl iodide to methane was determined to be the carbon–iodine bond cleavage [6]. Phenyl iodide has been studied on Cu(111) extensively [7–9] and on Ag(111) [10]. On both surfaces, phenyl iodide decomposes to iodine atoms and phenyl fragments, which couple to form biphenyl by 370 K.

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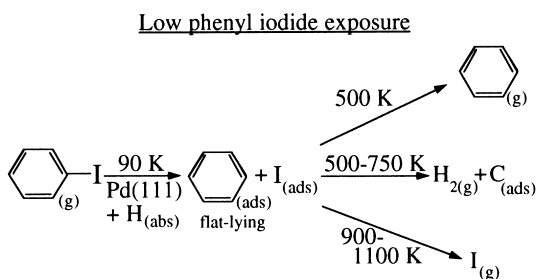


Fig. 1. Low phenyl iodide exposure reaction schematic on Pd(111).

We report the efficient production of benzene from phenyl iodide adsorbed on Pd(111) at 90 K. The reaction is probed using thermal desorption spectroscopy (TDS) and laser-induced thermal desorption (LITD). As shown in Fig. 1, at low initial phenyl iodide exposures only benzene, iodine, and hydrogen are observed (no phenyl iodide). At high initial exposures only phenyl iodide, benzene, and iodine are observed (no hydrogen), as shown in Fig. 2. Experiments using perdeuterated phenyl iodide indicate that benzene is formed from hydrogenation of adsorbed phenyl by sub-surface hydrogen by 143 K. Separate experiments show that adsorption of 10% of a monolayer of iodine atoms passivates the surface against decomposition of phenyl iodide and dehy-

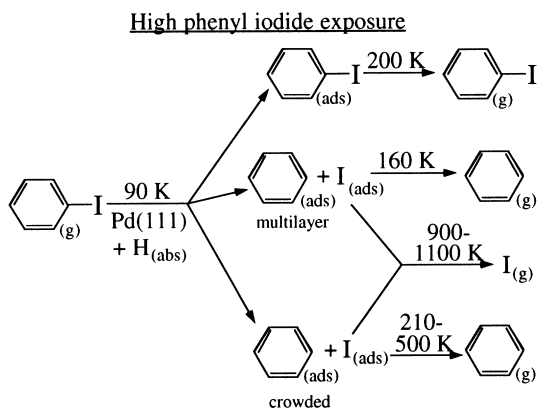


Fig. 2. High phenyl iodide exposure reaction schematic on Pd(111).

drogenation of benzene. Coupling to form biphenyl does not occur on Pd(111).

## 2. Experimental

The ultrahigh vacuum chamber, which has been described elsewhere [11,12], is equipped with an Auger electron spectrometer and low-energy electron diffraction for analysis of the single crystal surface cleanliness and a Fourier transform mass spectrometer (FTMS) for TDS and LITD experiments. The base pressure of the chamber is routinely below  $2 \times 10^{-10}$  Torr.

The palladium crystal (Aremco, 99.99%) is cleaned by  $\text{Ar}^+$  bombardment, oxygen treatments, and cycles of annealing to 1200 K. Impurities such as sulfur are monitored by Auger electron spectroscopy (AES), and the carbon contamination is checked by saturating the surface with oxygen at room temperature and observing the recombinative CO peak in TDS. Adsorbed carbon and oxygen combine and desorb as CO at 800 K, in contrast to the desorption of molecularly adsorbed CO at 500 K. The palladium crystal is deemed free of surface carbon when the 800 K recombinative CO TDS peak is no longer observed. The sample is flashed to 600 K to remove CO and surface hydrogen and recooled immediately before dosing. Iodine is removed after each experiment by heating the sample to 1100 K, which is above the desorption temperature of iodine on Pd(111). The absence of iodine on the surface is confirmed by AES.

The phenyl iodide (Aldrich, 98%) and the perdeuterated phenyl iodide (Aldrich, 98+%) are purified by vacuum distillation and freeze–pump–thaw cycles. Dosing is performed by backfilling the chamber with phenyl iodide while holding the temperature of the palladium crystal constant at 90 K. The exposures, given in langmuirs ( $1 \text{ L} = 1 \times 10^{-6}$  Torr s), are corrected by ion gauge sensitivities of 6.0 and 5.0 for phenyl iodide and benzene, respectively [13–15]. As explained later, AES indicates that saturation coverage of iodobenzene lying flat on the surface is achieved at approximately 10% of a monolayer (where one monolayer is one adsorbate per Pd atom), which corresponds

to a 1 L exposure, assuming a sticking coefficient of unity.

For experiments requiring the preadsorption of iodine atoms, the single crystal is exposed to 2.3 L of phenyl iodide and subsequently is heated to 700 K. As will be shown, the carbon–iodine bond dissociates at low temperatures and the adsorbed iodine blocks surface sites for decomposition. (Below the saturation coverage, some sites are still available and most of the hydrocarbon species on the surface decompose to leave carbon and hydrogen; however, above the saturation coverage all of the active sites are blocked, hence all of the carbon species desorb by 700 K to leave a carbon-free surface.) The absence of hydrocarbon fragments after heating a 2.3 L exposure of phenyl iodide is confirmed by the lack of hydrogen desorption under these conditions. AES spectra taken after this procedure confirm that 10% of a monolayer of iodine remains on the surface.

For TDS experiments, the sample is placed a few millimeters from an aperture in the FTMS cell. A copper flag placed between the cell and the sample produces a 2 mm diameter aperture through which desorption products must pass to enter the FTMS cell. The moveable flag reduces the detection of species desorbing from heating wires and the back of the sample. The sample is resistively heated at a rate of 3–4 K/s. Since FTMS is used for detection, a complete mass spectrum ( $m/z$  10–400) is obtained of the desorbing species every 2 s and the signal magnitude is in units of volt-seconds. For hydrogen-monitoring experiments, the magnetic field strength is decreased to approximately 0.1 T, since at the normal operating magnetic field of 0.6 T hydrogen cannot be observed with the current ADC rate.

For LITD experiments, the copper flag is removed to expose the entire sample to a 1.2 cm diameter aperture. The sample is held at a constant temperature and a Continuum Surelite Nd:YAG laser beam (1064 nm, 5 ns pulse width, 8 mJ/pulse) is focused onto a 1 mm diameter spot on the sample. The laser causes a localized heating rate of  $10^{11}$  K/s, which entropically favors desorption of compounds on the surface over decomposition. However, since desorption and decomposition are competing pathways, some decomposition may

still occur. Then the laser beam is focused onto another position on the surface and fired again. A complete mass spectrum ( $m/z$  10–400) is obtained after each laser shot with the FTMS. In LITD surveys, a series of spectra is obtained by holding the sample at a constant temperature for three or four laser shots, each at a different position, then stepping up the temperature and repeating the process to investigate a range of temperatures. An LITD survey effectively monitors the species remaining on the surface as a function of temperature, in contrast to the TDS experiment, which monitors the species desorbing from the sample at a given temperature.

Although LITD and TDS provide complementary information, the magnitudes of the respective signals are not directly comparable without calibration. First, desorption and decomposition compete, with the branching ratio dependent on initial temperature, heating rate, surface crowding, etc. Also, whereas TDS samples the species desorbing from most of the surface, LITD monitors species on a 1 mm region of the surface. Additionally, various FTMS parameters are set differently according to each type of experiment to accommodate the vastly differing transient pressure bursts produced. Temperature–time effects are also vastly different. Since the sample is held at a temperature for several minutes for LITD experiments, the temperature at which processes result in noticeable changes are much lower for LITD than for TDS, where the sample temperature is rapidly ramped.

FTMS is capable of monitoring either positive or negative ions. In positive-ion mode the trapping plate voltages are set at positive potentials. Positive ions are produced by pulsing a 70 eV electron beam through the center of the FTMS cell. In negative-ion mode the trapping plate voltages are set at negative potentials. For TDS, negative ions are formed using a 0.9 eV electron beam. In LITD, thermionic emission produces low-energy electrons from the palladium during laser heating [16]. Some desorbing neutrals form negative ions by capturing one of these electrons, so no electron beam is required.

Although all masses from  $m/z$  10–400 are monitored with FTMS, only a few masses are selected for plotting profile and survey graphs. These

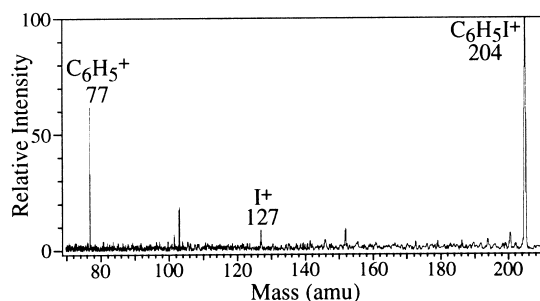


Fig. 3. Mass spectrum of gas-phase phenyl iodide. Note that  $m/z$  78 is not observed in the fragmentation pattern.

masses are extracted from the complete mass spectrum by establishing a noise level and using a peak-selecting routine that only selects peaks above that threshold. Any peaks below that level are plotted as zero signal. For phenyl iodide and benzene, the parent ions,  $m/z$  204 and  $m/z$  78, respectively, are used. The signal at  $m/z$  78, due to the isotopic abundance of  $^{13}\text{C}$  in  $m/z$  77, in the fragmentation pattern of phenyl iodide is negligible as shown in Fig. 3; therefore, the  $m/z$  78 parent ion of benzene was used without correction.

### 3. Results

When phenyl iodide is adsorbed on Pd(111) at 90 K and then heated, the observed desorption products are phenyl iodide, benzene, hydrogen, and iodine. TDS desorption profiles after exposing the Pd(111) surface to phenyl iodide are shown in Fig. 4a for phenyl iodide and in Fig. 4b for benzene. For exposures below 0.6 L (less than saturation coverage) no phenyl iodide desorption is observed. Above 0.6 L phenyl iodide desorbs at 200 K and the desorption peak does not saturate within the exposure range investigated. At low exposures benzene is observed to desorb around 500 K. As the initial phenyl iodide exposure is increased, the 500 K benzene peak dramatically broadens and shifts to lower temperatures. At 0.6 L, and above, the benzene desorption is dominated by a low temperature peak at 160 K. Under no circumstances does one observe hydrogen desorption indicative of adsorbed surface H atoms

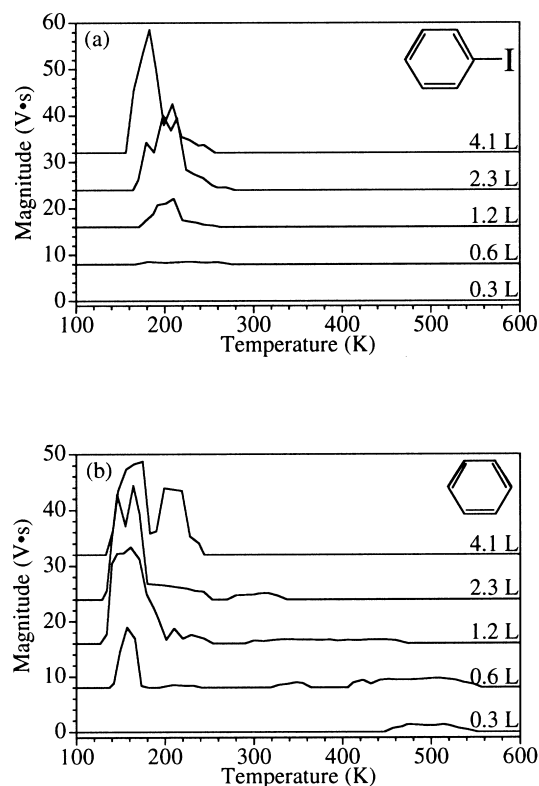


Fig. 4. Thermal desorption spectra of (a) phenyl iodide ( $m/z$  204) and (b) benzene ( $m/z$  78) after 0.3, 0.6, 1.2, 2.3, and 4.1 L initial exposures of phenyl iodide at 90 K on Pd(111).

(300–400 K). Only hydrogen from decomposition of hydrocarbons (500–750 K) or from sub-surface is observed (Fig. 7).

In the negative ion TDS experiment, for the 1.0 L initial exposure of phenyl iodide shown in Fig. 5 the iodine anion is observed at about 210 K and between 938 and 1075 K. The peak at 210 K matches the desorption peak of phenyl iodide observed in the positive ion TDS experiments; therefore, the iodine comes from desorbing phenyl iodide. Compounds containing a halogen typically undergo dissociative attachment of an electron to form the halogen anion [17,18]. Studies of the electron capture of benzene derivatives demonstrate that the onset of dissociative electron capture occurs below 0.3 eV electron energy for halogenated benzenes [19–21]. In particular, phenyl iodide is observed to fragment upon capturing

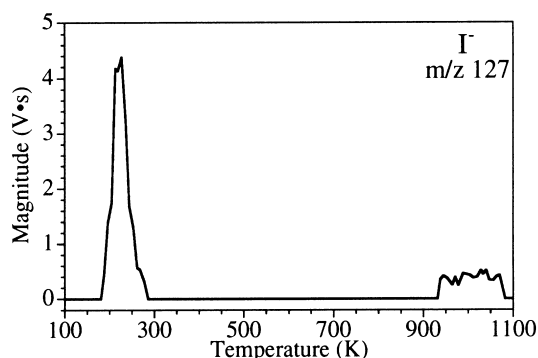


Fig. 5. Thermal desorption negative ion spectrum after a 1.0 L initial exposure of phenyl iodide at 90 K on Pd(111).

electrons at 0 eV, resulting in a significant signal for  $I^-$  [19]. The iodine species desorbing between 938 and 1075 K is probably  $I_2$  or I atoms. Hydrogen iodide is an unlikely candidate for the species desorbing above 900 K, since surface hydrogen desorbs around 350 K from clean Pd(111) [22]. The facile dissociation of halogens after electron capture makes identification of the parent compound problematic. After heating to 1100 K, all iodine-containing compounds have desorbed, leaving an iodine-free Pd(111) surface, as confirmed by AES.

The LITD surveys shown in Fig. 6 correlate well with the TDS studies at similar initial exposures of phenyl iodide. In Fig. 6a, for a 0.3 L LITD survey, no phenyl iodide is observed on the surface even at 90 K. Benzene is observed immediately at 90 K and disappears around 500 K. The LITD benzene signal has been shown to increase as the sample approaches the desorption temperature of benzene due to an increase in the efficiency of laser desorption over decomposition [23]. This effect can be calibrated by adsorbing benzene and monitoring the LITD signal versus temperature when no other chemistry is occurring. After correction, the benzene signal remains relatively constant throughout at this coverage. In the LITD experiments performed after higher initial exposures, shown in Fig. 6b and c, phenyl iodide disappears around 185 K, and the benzene signal drops significantly by 160 K and disappears by 350 K. In a negative-ion mode LITD survey, for a 1.9 L initial

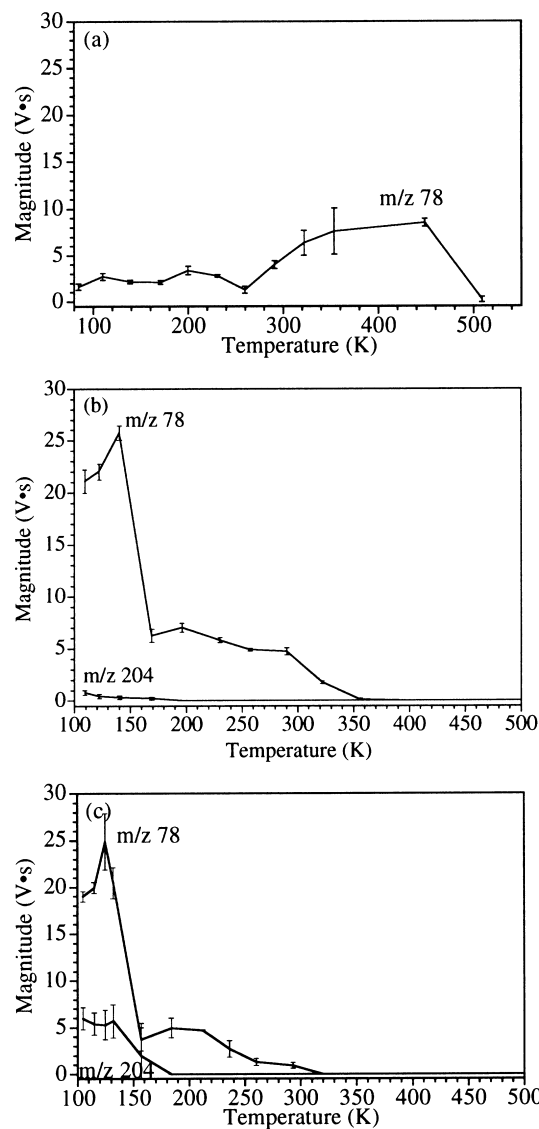


Fig. 6. LITD surveys of phenyl iodide ( $m/z$  204) and benzene ( $m/z$  78) after (a) 0.3 L, (b) 1.8 L, and (c) 3.3 L initial exposures of phenyl iodide at 90 K on Pd(111).

exposure of phenyl iodide the iodine anion is observed between 83 and 114 K due to the gas-phase fragmentation of phenyl iodide after desorbing under the laser from the surface. The disappearance of the phenyl iodide and the benzene signals in the LITD experiments occurs at approximately the same temperature as the desorption of

phenyl iodide and benzene observed in TDS. The temperatures differ somewhat between the two types of experiment due to the different heating procedures used (rapid constant temperature ramp in TDS leads to higher temperatures versus slow step-wise heating in LITD). Significantly, no signal corresponding to the formation of biphenyl ( $m/z$  154) is observed in either TDS or LITD experiments, indicating that no coupling of phenyl groups occurs on Pd(111).

#### 4. Discussion

Since no phenyl iodide is observed on the Pd(111) surface at low initial coverages, as shown by the 0.3 L LITD survey in Fig. 6a, phenyl iodide most likely adsorbs dissociatively at 90 K. The benzene formed from phenyl groups on the surface desorbs at around 500 K, which corresponds to the desorption temperature of flat-lying benzene [24,25]. In previous studies of benzene desorption from clean Pd(111), the 520 K desorption peak saturates as the initial benzene exposure is increased and low temperature peaks grow in Refs. [24,25]. In contrast, as the initial exposure of phenyl iodide on Pd(111) is increased, the 500 K benzene desorption peak (from phenyl iodide decomposition) shifts to lower temperatures and eventually is completely lost as benzene desorption begins to occur in a low temperature (160 K) peak.

A low initial exposure (less than saturation coverage) of phenyl iodide yields a hydrogen desorption spectrum typical of that observed from the decomposition of flat-lying benzene [24,25]. Hydrogen desorption occurs at 550 K and extends out to 750 K, as shown in Fig. 7 of TDS monitoring hydrogen evolution after a 0.3 L initial exposure of phenyl iodide. The absence of the 350 K recombinative surface hydrogen peak [22] indicates that there is no surface hydrogen and that no carbon–hydrogen bonds break below 500 K; thus, only carbon–iodine bonds are cleaved. Therefore, it is postulated that sub-surface hydrogen reacts with the adsorbed phenyl groups to form benzene. Hydrogenation of phenyl groups without additional hydrogen dosed on the surface of Pd(111) was also observed for fluorobenzene

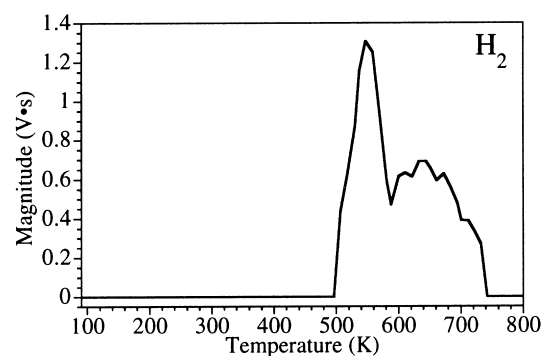


Fig. 7. Thermal desorption spectrum monitoring hydrogen ( $m/z$  2) evolution after a 0.3 L initial exposure of phenyl iodide at 90 K on Pd(111).

and chlorobenzene by Aarts and Phelan [13]. Experiments with perdeuterated phenyl iodide support hydrogenation by sub-surface hydrogen. In Fig. 8, individual spectra from gas-phase  $C_6D_5I$  (Fig. 8b) and from a TDS experiment using  $C_6D_5I$  (Fig. 8a) are shown. TDS of a 1.0 L initial exposure of perdeuterated phenyl iodide results in  $C_6D_5I$  ( $m/z$  209) desorbing between 181 and 280 K, with a maximum at 191 K, and  $C_6D_5H$  ( $m/z$  83)

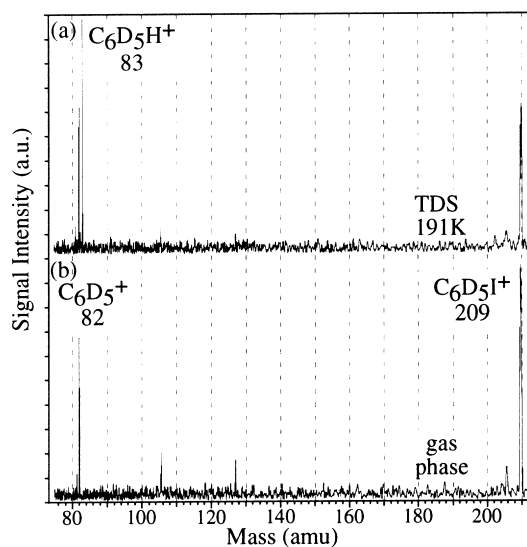


Fig. 8. Individual mass spectra for (a) a TDS of a 1.0 L initial exposure of perdeuterated phenyl iodide on Pd(111) at 191 K and (b) gas-phase perdeuterated phenyl iodide. Only  $m/z$  75–215 are shown.

desorbing between 143 and 270 K, with a maximum at 160 K, and between 302 and 533 K. A single mass spectrum from the TDS at 191 K (Fig. 8a) shows that the only benzene product formed is  $C_6D_5H$  ( $m/z$  83); thus, phenyl groups do not extract hydrogen from other phenyl groups or from phenyl iodide to form benzene. Similar results were obtained by Chen and Winograd with methyl iodide and deuterated methyl iodide on Pd(111) [6], in which they also observed only one methane product,  $CD_3H$ , formed by 200 K from  $CD_3I$ . In the present studies, it is evident that the reaction of sub-surface hydrogen with phenyl occurs by 143 K. This sub-surface hydrogen is probably replenished from the bulk during cooling.

At 0.6 L, and higher exposures, phenyl iodide begins to desorb at 200 K. Phenyl iodide most likely adsorbs flat on Pd(111) for submonolayer coverages, similar to its geometry on Cu(111) [7]. The flat-lying phenyl iodide decomposes to yield iodine and benzene on the surface. However, a high concentration of adsorbates may cause the phenyl iodide to adsorb tilted. It has been shown that, for high coverages of phenyl iodide on Cu(111), a 'bilayer adsorption model' fits the data: flat-lying phenyl iodide in the first layer and tilted phenyl iodide in the second layer [8,9]. The interaction between the surface and tilted phenyl iodide should be weaker than that for flat-lying phenyl iodide and lead to desorption rather than decomposition. Additionally, the iodine adsorbed on the surface can inhibit the decomposition of further amounts of phenyl iodide by blocking active sites [26].

Additionally, at higher exposures of phenyl iodide the 500 K benzene desorption peak shifts to lower temperatures. The progression of the higher temperature peak may be due to crowding on the surface. Phenyl iodide decomposition yields iodine and flat-lying benzene. As the surface is exposed to increasing amounts of adsorbates, the benzene formed on the surface becomes more crowded and desorbs at lower temperatures, as observed by Tysoe et al. [25] for benzene on clean Pd(111). Additional evidence for crowded flat-lying benzene molecules is the lack of hydrogen desorption at higher exposures. Tysoe et al. [25] determined that hydrogen desorption from the

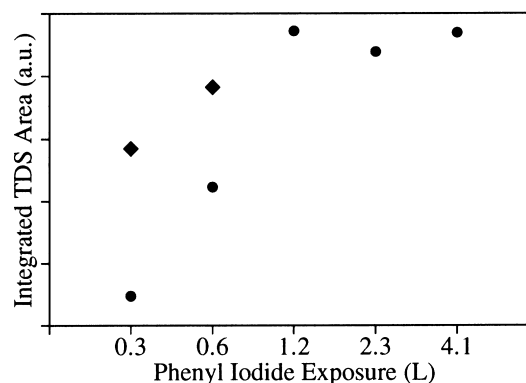


Fig. 9. Relative amounts of benzene that desorbs after phenyl iodide exposures at 90 K on Pd(111). The relative amounts are determined by integrating the  $m/z$  78 TDS peaks (●) and adjusting for the decomposition of some flat-lying benzene (◆).

benzene decomposition on clean Pd(111) does not occur when there are no available surface sites around the benzene molecules. A 1.1 L initial exposure of phenyl iodide produces no hydrogen during a TDS experiment, indicating that no benzene decomposes. Therefore, any flat-lying benzene present on the surface is crowded and desorbs at a temperature lower than 500 K. Eventually the benzene can tilt, as observed by Hoffmann et al. [27] for benzene on clean Pd(111), to accommodate more phenyl iodide on the surface and desorb at around 210 K.

The dominant benzene desorption peak at higher exposures of phenyl iodide occurs at around 160 K. Since the temperature is approximately 20 K higher than the temperature at which multilayer benzene desorbs from clean Pd(111) [28], we attribute this peak to benzene that interacts with coadsorbed iodine. As described later, Fig. 10a shows that the benzene desorption peak from Pd(111) precovered with iodine resembles the benzene desorption from phenyl iodide decomposition on clean Pd(111). A similar low temperature peak has been obtained by Lin and Bent [29] for octane adsorbed onto iodine-precovered Cu(111) versus clean Cu(111).

The relative amount of benzene formed after different initial phenyl iodide exposures can be estimated by integration of the benzene TDS traces. Fig. 9 shows that benzene formation satu-



rates by 1.2 L. The amount of benzene observed at low initial phenyl iodide exposures (0.3 and 0.6 L) must be corrected for the decomposition of flat-lying benzene, some of which desorbs above 400 K. It has been shown that up to a 0.05 monolayer coverage of flat-lying benzene decomposes [25]. If we assume that a total adsorbate coverage of 0.05 monolayers or higher is necessary for benzene to desorb in this system, that coverage corresponds to a 0.25 L exposure of phenyl iodide. Thus, the integrated areas of the high temperature ( $T > 400$  K) portion of the benzene TDS traces are adjusted to account for the amount decomposing. The amount of benzene formed saturates between 0.6 and 1.2 L. Also, in this range the 500 K benzene desorption peak begins to shift to lower temperatures, indicating an increase in crowding.

AES after warming separately 1.5 and 2.5 L initial exposures to 700 K shows residual surface iodine saturation at about 10% of a monolayer. Assuming that only the first layer of phenyl iodide decomposes, the highest percentage of iodine left on the surface after the desorption of all other species approximates the saturation coverage of phenyl iodide. Therefore, flat-lying phenyl iodide saturates the surface at about 0.1 monolayers. Additionally, the amount of flat-lying benzene on Pd(111) saturates at about 13% of a monolayer [25]; so, after taking into account the relative van der Waal's radii, the maximum amount of flat-lying phenyl iodide, or a saturation coverage, should be about 10% of a monolayer on Pd(111).

The effect of iodine atoms on the chemistry of phenyl iodide and benzene is shown in Fig. 10. Benzene and phenyl iodide are dosed separately onto an iodine-precovered Pd(111) surface prepared as described previously. The iodine comprises about 10% of the surface according to the relative intensities of the AES signals for palladium and iodine. TDS after a 1.0 L exposure of benzene on the iodine-precovered surface, shown in Fig. 10a, results in almost complete desorption of benzene at 150 K with only a small amount of benzene desorbing between 300 and 500 K, whereas 1 L of benzene desorbs and decomposes between 400 and 500 K on a clean Pd(111) surface [24,25]. The iodine-precovered surface can still

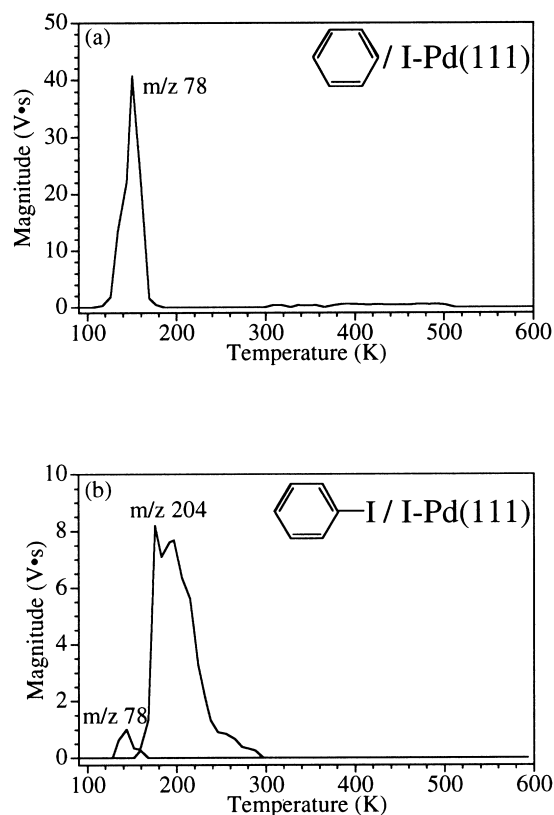


Fig. 10. Thermal desorption spectra on a 10% iodine covered Pd(111) surface after (a) a 1.0 L initial exposure of benzene, and (b) a 1.0 L initial exposure of phenyl iodide at 90 K.

accommodate a small amount of flat-lying benzene; however, the benzene is crowded and desorbs before 520 K. Most of the benzene interacts with the iodine and desorbs at 150 K. TDS after a 1.1 L exposure of phenyl iodide on iodine-precovered Pd(111), shown in Fig. 10b, produces predominantly phenyl iodide desorption at 190 K and only a small desorption peak for benzene at 145 K with no benzene desorbing at higher temperatures. Very little benzene is formed from the phenyl iodide; therefore, the iodine inhibits the decomposition of phenyl iodide to a large extent. It is likely that decomposition takes place only at defects in the iodine overlayer.

No biphenyl desorption is observed, in contrast to the chemistry of phenyl iodide on Cu(111) [7–9] and Ag(111) [10]. Phenyl iodide decomposes

on Cu(111) to phenyl groups around 175 K, which are stable above 320 K and couple to form biphenyl by 370 K [7–9]. Submonolayer coverages of phenyl iodide on Ag(111) have been observed to decompose to phenyl groups, which then combine to form biphenyl by 370 K [10].

## 5. Conclusion

Phenyl iodide dissociatively adsorbs at 90 K on Pd(111). The reaction is probed using TDS and LITD. At low initial phenyl iodide exposures only benzene, iodine, and hydrogen are observed (no phenyl iodide). At high initial exposures only phenyl iodide, benzene, and iodine are observed (no hydrogen). Experiments with perdeuterated phenyl iodide indicate that benzene is formed from hydrogenation of adsorbed phenyl by sub-surface hydrogen by 143 K.

At low initial coverages of phenyl iodide small amounts of benzene desorb at about 500 K and the rest dehydrogenates above 500 K to produce H<sub>2</sub>. The first 10% of a monolayer (close to saturation) of phenyl iodide decomposes upon adsorption at 90 K. Higher initial coverages lead to intact desorption of phenyl iodide at 190–200 K, as well as decomposition. Higher initial coverages of phenyl iodide also result in desorption of benzene at lower temperatures, with an increased yield at 160 K. Separate experiments show that adsorption of 10% of a monolayer of iodine atoms passivates the surface against decomposition of phenyl iodide and dehydrogenation of benzene. Additionally, on the iodine-precovered palladium surface, phenyl iodide desorbs at 190 K and benzene desorbs at 150 K, as observed for these species from higher coverages of phenyl iodide alone on clean Pd(111). Coupling to form biphenyl does not occur on Pd(111).

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