Conclusions

In reporting the gas-phase acidities of a variety of silanols, we have examined the effect of substituents on acidity. Alkyl substitution leads to decreased acidity, in contrast to alkyl substitution effects in alcohols. Polar substituents increase silanol acidity, with chlorine and fluorine having the greatest effect. The substituent effects are best understood in terms of polarizability and inductive contributions. With alkyl substitution, in which the polarizability and inductive effects are opposed, the polarization is attenuated relative to the inductive effect because of its more critical dependence on distance. With other substituents, these two effects tend to both lead to increases in acidity.

Surface-Induced Heterocycle Formation: Sulfur Atom Abstraction during Cyclization

Andrew J. Gellman

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. Received June 18, 1990. Revised Manuscript Received February 1, 1991

Abstract: We have studied the mechanism of a novel cyclization reaction in which acetylene abstracts sulfur from the Pd(111) surface in the form of thiophene. The proposed mechanism is one in which adsorbed acetylene first dimerizes to form a C_4H_4 intermediate which is then capable of abstracting atomic sulfur to form thiophene. The appearance of thiophene in the gas phase is then rate limited by thiophene desorption kinetics. This sequential mechanism has also been proposed for acetylene cyclotrimerization to benzene on the clean Pd(111) surface. Thiophene formation from acetylene is sensitive to both the surface sulfur coverage and the temperature at which the sulfur overlayer is produced. The reaction of a C_4H_4 species produced from *cis*-3,4-dichlorocyclobutene exhibits exactly the same sensitivity to surface characteristics and hence is identified as the intermediate produced by acetylene dimerization. We discuss the potential of this chemistry as a process for the regeneration of catalytic surfaces deactivated by sulfur contamination.

1. Introduction

There are a number of important cyclization reactions such as ethylene epoxidation and alkane dehydrocyclization that are catalyzed by metallic surfaces.[1,2] One novel reaction that has received attention over the past 5 years is the cyclotrimerization of acetylene on palladium surfaces. The first observations of this reaction under ultra-high-vacuum (UHV) conditions were reported by three groups in 1983,[3-5] and since then it has received careful study by Patterson et al.[6,7] The same reaction has also been observed on single-crystal surfaces of palladium at high pressures,[8,9] on Ni(111) surfaces,[10,11] and on the Cu(110) surface.[12] This paper presents a study of an important variant on this reaction in which sulfur is abstracted from the palladium surface in the form of thiophene.[13] Its importance stems from the fact that sulfur abstraction is necessary for regeneration of sulfur-contaminated catalytic surfaces. Furthermore, the fact that sulfur rather than acetylene is the third component being incorporated into the ring allows easier mechanistic study of the reaction.

The cyclotrimerization of acetylene to benzene on the clean Pd(111) surface occurs following acetylene adsorption at low temperatures (<150 K). During a thermal desorption experiment benzene desorption is observed both at 250 K and then again at 500 K. Patterson et al. have performed a comprehensive mechanistic study of this reaction. Using mixtures of C_2H_2 and C_2D_2 they have shown that the reaction occurs without carbon–carbon or carbon–hydrogen bond breaking. Using *cis*-3,4-dichlorocyclobutene ($C_4H_4Cl_2$) as a precursor, they have produced a C_4H_4 intermediate on the Pd(111) surface which cyclizes with C_2D_2 to yield benzene-d_2, clearly indicating that the reaction can occur via a sequential mechanism involving initial dimerization followed by cyclization.[6,7] Furthermore, molecular beam kinetics studies of the cyclotrimerization reaction revealed a C_4 species desorbing into the gas phase,[3] and catalysis of this reaction at high pressures by supported Pd particles has been found to produce 1,3-butadiene.[14] Most recently, a reaction similar to the one studied in this work has been observed to produce furan by heterocyclization of acetylene with oxygen atoms.[15] Vibrational spectra of the C_4H_4 species generated during decomposition of $C_4H_4Cl_2$ have been obtained with use of HREELS.[16] Comparison with vibrational spectra of several inorganic complexes indicates that the C_4H_4 intermediate is a cyclic compound with its ring plane tilted away from the surface normal. Obvious candidates are a metallapentacycle or a palladium-substituted cyclobutene.

There are a number of inorganic and organometallic complexes that either catalyze cyclization reactions[17-20] or will react with other reagents to form cyclic species.[21,22] One of the best known

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of these complexes is CpCo(CO)$_2$ which is capable of cyclizing a wide variety of substituted acetylenes and α,Ω-diynes.[17-19] The mechanism is one in which the metal center is first complexed with two acetylenes in the form of a metallapentacycle which has been isolated as a stable intermediate in a number of cases.[19] It has also been demonstrated that the initial acetylene dimerization reaction does not lead to or proceed via the formation of a cyclobutadiene ligand on the metal.[20]

In addition to reactions producing benzenes there are a number of inorganic complexes that will produce heterocycles such as thiophenes. One example is a reaction between a rhodium pentacycle and sulfur yielding a thiophene.[21,22] The common thread among these reactions is that they all appear to involve cyclic intermediates which include the metal center implying that the analagous intermediate in the surface induced cyclization reactions may well be a metallapentacycle. Another example is the thermolysis of a solid with the formula (C$_4$(CH$_3$)$_4$)$_2$Ni$_2$WS$_5$ which yields tetramethylthiophene.[23] Although it is not certain, the reacting species in this case may be a cyclobutadiene. An important point about all these reactions is that at relatively low temperatures they result in the incorporation of heteroatoms such as sulfur into volatile cyclic organic compounds. This is the type of chemistry needed to remove heteroatoms from catalytic surfaces and to regenerate catalysts that have been contaminated by sulfur.

The problems of sulfur poisoning of catalysts and catalyst regeneration have been addressed by a number of groups.[24,25] For the most part metal–sulfur bonds are fairly strong and removal of sulfur from metal surfaces requires extreme conditions. Efforts have been made to use oxygen, hydrogen, and steam as agents for either reduction to H$_2$S or oxidation to SO$_2$. These require both high temperatures (700–1100 K) and pressures and the oxidation reaction then requires subsequent high-temperature reduction of the catalyst. From a practical perspective the use of high temperatures is costly and in the case of highly dispersed catalysts runs the risk of reducing the catalytic surface area by sintering. The use of surface organic chemistry of the type that we have observed poses a potential low-temperature route to sulfur removal from metals. In principle, any volatile sulfur containing organic product which can be removed from the catalyst in the gas phase would be useful. In practice thermodynamics and the strength of the metal–sulfur bond will limit the range of viable reactants and products. Clearly reactions leading from reactants with high heats of formation to stable aromatics are obvious choices.

Sulfur overlayers on the Pd(111) surface can be produced by either adsorption and decomposition of H$_2$S[27] or adsorption of S$_2$.[28] At 0.33 monolayer coverage and temperatures <400 K the sulfur overlayer forms a $(\sqrt{3}\times\sqrt{3})R30°$ lattice with respect to the substrate. A structural examination of this overlayer with LEED has shown that the atoms are situated in the 3-fold hollows with a metal–sulfur bond length of 2.2 Å.[27] Heating this surface above 400 K results in irreversible loss of the $(\sqrt{3}\times\sqrt{3})R30°$ lattice and the formation of a structure with $(\sqrt{7}\times\sqrt{7})R19°$ periodicity with respect to the substrate.[28] No structural information is available concerning the high-temperature $(\sqrt{7}\times\sqrt{7})R19°$ lattice. While we do not know the details of the structural differences between the high- and the low-temperature sulfur phases it is clear that there are distinct differences in the cyclization reactions on the two surfaces.

2. Experimental Section

The experiments reported in this paper have been performed in two ultra-high-vacuum chambers each equipped for surface preparation with

ion sputtering and gas dosers, surface analysis with Auger electron spectroscopy (AES), and low energy electron diffraction (LEED). Each is pumped to a vacuum in the low 10^{-10} Torr range.

Two Pd single crystals were used, each with the (111) surface exposed and polished with standard techniques. The contaminants that had to be removed from the surface during the course of this work were sulfur, carbon, oxygen, and chlorine. Both oxygen and chlorine can be removed by heating to induce desorption at 800 and 600 K, respectively.[29,30] Sulfur was removed from the surface by sputtering the crystal with an Ar$^+$ ion current of ∼10 μA at 1000 eV for periods of roughly 10 min. During sputtering the crystal was usually annealed at a temperature of 1000 K for 1–2 min to induce segregation of contaminants. Following sputtering the crystal was annealed again to remove beam damage and produce a well-ordered surface. Removal of carbon from the surface was achieved by exposure to oxygen at high temperatures (900–1000 K). The detection of carbon on the surface is hampered by the Pd Auger transition at 270 eV. Our test for cleanliness was to adsorb oxygen on the surface at low temperature (130 K) and monitor the desorption of CO from the surface during heating. The criterion for cleanliness of carbon was that the amount of CO desorbing should be less than 1% of the room temperature saturation CO coverage.

One important observation was that following adsorption and desorption of acetylene there was clearly some carbon left on the surface or in the near surface region of the crystal. Several repetitions of the oxygen adsorption/desorption treatment were necessary to clean the surface. We also noted that if during desorption of acetylene the crystal is heated to only 600 K this carbon residue will modify the surface cyclotrimerization chemistry of any further acetylene that is adsorbed. If the surface is heated to >1000 K then although there is some carbon in the near surface region it does not have any apparent effect on the cyclotrimerization reaction. In all cases reported here the sample was heated to 1050 K during desorption in order to remove the effects of residual carbon.

To remove acetone the acetylene was purified by sublimation from a molecular sieve cooled to 77 K. The purity of the acetylene was checked with use of the mass spectrometer in the UHV chamber. The sulfur films were produced by adsorption and decomposition of H$_2$S. The samples of thiophene and cis-3,4-dichlorocyclobutene were purified of low vapor pressure contaminants by repeated freeze–pump–thaw cycles. Gases were introduced into the UHV chamber through leak valves fitted with glass capillary array dosers. The crystal surface was positioned roughly 5 mm from the front face of the capillary arrays allowing saturation coverage of the crystal surface with relatively low exposures of gas.

The sample was spotwelded between two platinum wires connected to two liquid nitrogen reservoirs at the end of a UHV manipulator. Temperature measurement was made with use of a chromel–alumel thermocouple also spotwelded to the side of the sample. The sample could be cooled to 120 K and heated resistively to temperatures approaching the melting point. Both temperature measurement and heating current were controlled by a computer using both proportional and derivative feedback to allow accurate control of the sample heating rate during desorption measurements and annealing treatments.

Following sample exposure to the adsorbate the desorption measurements were made with a Dycor M200M quadrupole mass spectrometer. The mass spectrometer was housed in a shield with a 0.375 in. o.d. tube as the front aperture into the ionizer. The sample was positioned within about 1 mm of the aperture tube prior to heating. Heating rates were kept constant at 10 K/s for all experiments and initial temperatures were in the range 120–140 K.

3. Results

3.1. Sulfide Film Formation. Throughout the work described here we have used two distinct sulfide films on the Pd(111) surface. These have been referred to as the "high temperature" and the "low temperature" overlayers. Both have been produced by repeated exposure of the surface to H$_2$S followed by heating to induce dissociation and desorb hydrogen. The surface was heated to 1050 K to produce the high-temperature overlayer and 350 K to produce the low-temperature overlayer. In the case of the low-temperature overlayer we determined that all hydrogen had been removed from the surface by monitoring hydrogen thermal desorption during heating from 120 to 1050 K. No hydrogen evolution was observed from the surface, indicating that all had desorbed during prior heating to 350 K.

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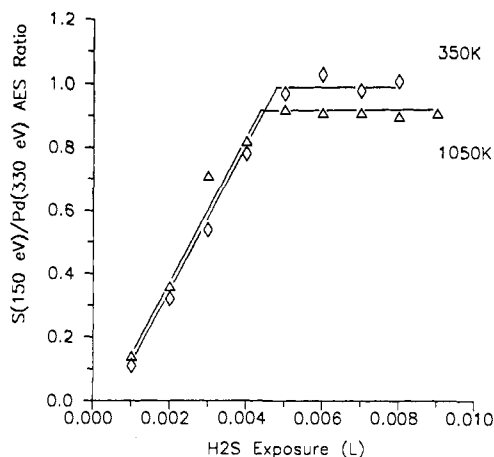**Figure 1.** The S_{150eV}/Pd_{330eV} Auger intensity ratio during sequential exposure of the Pd(111) surface to H_2S. Immediately following each exposure the sample was heated to either 1050 K (high temperature) or 350 K (low temperature) for 60 s, to dissociate H_2S and desorb hydrogen.

Figure 1 plots the S_{150eV}/Pd_{330eV} Auger peak height ratio during repeated exposure to H_2S and heating to either 350 or 1050 K. The surface takes up sulfur in the process until a saturated overlayer is produced. At this point further exposure to H_2S results in reversible molecular adsorption followed by desorption rather than decomposition during heating. The Auger ratio for the high-temperature overlayer is slightly lower than that of the low-temperature overlayer. It is also the case that on heating the saturated low-temperature overlayer to 1050 K the intensity of the sulfur Auger signal decreases to the value observed for films actually formed by sequential exposure to H_2S and immediate heating to 1050 K. This decrease in the intensity of the Auger signal is not accompanied by any sulfur desorption. The only other indication of difference between the two surfaces is that there is a change in the long-range order of the overlayer. The overlayer produced at low temperature has $(\sqrt{3}\times\sqrt{3})R30°$ periodicity and a sulfur coverage of 1/3 monolayer. We have found that by repeated exposure of the surface to H_2S (total exposure of 0.1 L with capillary array dosers) and heating to low temperature (350 K) one can produce the $(\sqrt{7}\times\sqrt{7})R19°$ overlayer. Alternately, the $(\sqrt{7}\times\sqrt{7})R19°$ overlayer can be formed by annealing the $(\sqrt{3}\times\sqrt{3})R30°$ overlayer to temperatures in excess of 400 K. This occurs without a change in sulfur coverage and is probably the result of formation of islands of $(\sqrt{7}\times\sqrt{7})R19°$ structure. Heating to high temperatures results in a decrease in the sulfur coverage as measured with Auger spectroscopy. The quality of the electron diffraction pattern produced by the $(\sqrt{7}\times\sqrt{7})R19°$ lattice depends on the temperature to which the surface has been heated. The sharpest diffraction patterns are produced by surfaces that have been heated to 500–800 K, whereas a surface that has been heated to 1050 K exhibits diffraction with high background intensity.

3.2. Thiophene Formation from C_2H_2. Figure 2 displays the thermal desorption of thiophene following adsorption of acetylene on a Pd(111) surface which has been sulfided at high temperature. Thiophene desorption occurs over a broad temperature range from 280 to 420 K. Benzene desorption is also observed and occurs over a slightly broader temperature range (260–500 K) with kinetics that are clearly different from those observed on the clean surface. Both products have been identified by examination of their mass spectral fragmentation patterns. The reaction path leading to the formation of gas-phase thiophene is a minor one. Comparison with the amount of thiophene adsorbed in a saturated monolayer indicates that the amount of thiophene produced following adsorption of acetylene corresponds to roughly 0.1% of a monolayer. Further adsorption of acetylene on the surface following the initial desorption experiment results in the formation of an equivalent amount of thiophene. Auger spectroscopy does not indicate any measurable decrease in the sulfur coverage following any one given adsorption/desorption cycle; however,
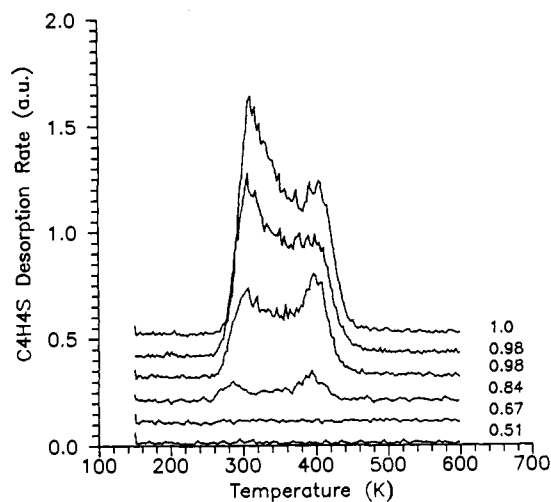

Figure 2. Thiophene desorption from the high-temperature (1050 K) Pd(111)/S surface following acetylene adsorption (0.05 L at 120 K). The TDS spectra are shown at various sulfur coverages. The sulfur coverages are quoted as fractions of the saturation value obtained by adsorption of H_2S followed by heating to 1050 K.
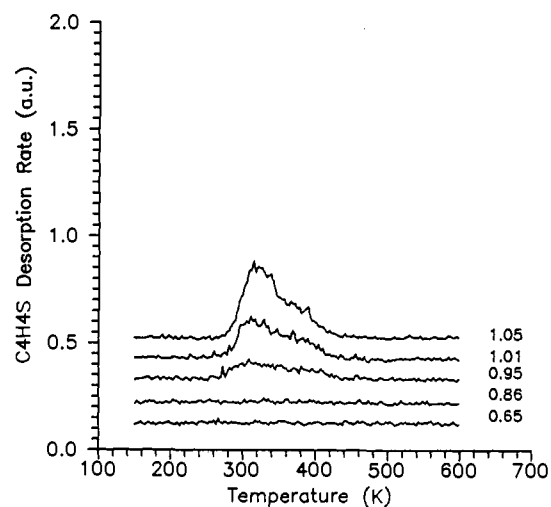

Figure 3. Thiophene desorption from the low-temperature (350 K) Pd-(111)/S surface following exposure to 0.05 L of acetylene at 120 K. The TDS spectra are shown at various initial sulfur coverages quoted as fractions of the saturation value obtained by adsorption of H_2S followed by heating to 350 K.

repeated acetylene adsorption followed by thiophene desorption will result in small but measurable decreases in the intensity of the sulfur Auger signal.

Acetylene heterocyclization to yield thiophene is sensitive to both the initial coverage of sulfur on the surface and the temperature at which the sulfur overlayer has been produced. Figure 2 shows the thermal desorption of thiophene following acetylene adsorption on the high–temperature Pd(111)/S surface at various sulfur coverages. The exposure of 0.05 L (1 L = 10^{-6} Torr·s) with use of the doser is sufficient to saturate the reaction path leading to the formation of thiophene. At low coverages there is no thiophene formation although benzene is produced, as on the clean surface. The onset of thiophene formation occurs at coverages approaching saturation. It is interesting to note that the temperature range over which thiophene desorbs does not depend on sulfur coverage. Figure 3 shows the thiophene desorption spectra following acetylene adsorption on the low-temperature Pd(111)/S surface. These exhibit the same dependence on sulfur coverage; however, the total amount of thiophene desorbing from the surface is roughly a factor of 5 less than the amount produced on the high-temperature phase. Again it is worth noting that on both the high- and low-temperature surfaces the desorption kinetics are essentially identical in the sense that, although the yield of
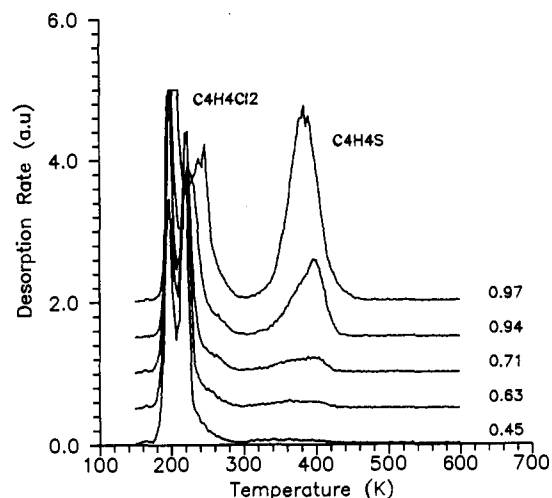
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Figure 4. Thiophene desorption following exposure of the high-temperature (1050 K) Pd(111)/S surface to cis-3,4-dichlorocyclobutene (C$_4$-H$_4$Cl$_2$). The thermal desorption spectra are shown at various initial coverages of sulfur quoted as fractions of the saturation value obtained by H$_2$S adsorption followed by heating to 1050 K. The low-temperature peaks are due to C$_4$H$_4$Cl$_2$ desorption. C$_4$H$_4$Cl$_2$ yields a fragment having a mass of 84 amu during electron impact ionization.

Figure 5. Thiophene desorption following adsorption of C$_4$H$_4$Cl$_2$ on both the high- and the low-temperature Pd(111)/S surfaces. The low-temperature peaks are 84 amu fragments of C$_4$H$_4$Cl$_2$ desorbing from the surface. Sulfur coverages are at the saturation values produced by H$_2$S adsorption followed by heating to either 350 or 1050 K.

Figure 6. Thiophene desorption following adsorption of acetylene, cis-3,4-dichlorocyclobutene, and thiophene on the high-temperature (1050 K) sulfided Pd(111) surface. The spectra have been normalized to the same amplitude at 380 K.

thiophene differs, desorption occurs in the same temperature range.

3.3. Thiophene Formation from C$_4$H$_4$Cl$_2$. We wish to decide whether it is reasonable to describe the mechanism of thiophene formation in terms of an acetylene dimerization step followed by sulfur atom incorporation into a ring. Using the same precursor as has been used in the study of acetylene cyclotrimerization we have looked for the formation of thiophene from cis-3,4-dichlorocyclobutene on the sulfided Pd(111) surface.[7] Figure 4 shows the desorption of thiophene following adsorption of C$_4$H$_4$Cl$_2$ on the high-temperature Pd(111)/S surface. Desorption spectra are shown at various initial sulfur coverages. It is clear that the C$_4$H$_4$ intermediate will cyclize with sulfur to produce thiophene. Thiophene has been identified again by its mass spectral fragmentation pattern and is observed desorbing in the temperature range 350–400 K. The peaks at low temperature have been identified as fragments of C$_4$H$_4$Cl$_2$, some of which adsorbs reversibly and desorbs in the temperature range 180–250 K. The important feature of Figure 4 is that thiophene formation from the C$_4$H$_4$ intermediate produced by C$_4$H$_4$Cl$_2$ decomposition exhibits the same dependence on sulfur coverage as the formation of thiophene from acetylene. Again the kinetics do not appear to depend on sulfur coverage except that there is a critical coverage below which the reaction will not occur.

The heterocyclization reactions of acetylene and C$_4$H$_4$ with sulfur not only exhibit the same dependence on sulfur coverage but also exhibit the same sensitivity to the temperature at which the sulfur overlayer was produced. Figure 5 compares thiophene desorption following exposure of C$_4$H$_4$Cl$_2$ to both the high- and the low-temperature Pd(111)/S surfaces. It is clear that thiophene desorption is occurring with the same kinetics but with different total amounts of thiophene being produced. Again it is the high-temperature sulfided surface that generates the greatest amount of thiophene.

3.4. Thiophene Desorption Kinetics. It is clear from the above work that the upper temperature limit of thiophene desorption is independent of whether it is produced from acetylene or C$_4$-H$_4$Cl$_2$. In Figure 6 we compare the desorption of thiophene from the high-temperature Pd(111)/S surface following adsorption of acetylene, C$_4$H$_4$Cl$_2$, and thiophene. We have taken care to reproduce heating rates and starting temperatures as closely as possible and the three spectra have been scaled to have roughly equal amplitudes at 380 K. It is clear that the desorption kinetics at the high end of the temperature range in which thiophene is desorbing are identical in all three cases. It appears most likely that at these temperatures thiophene exists on the surface and that its appearance in the gas phase is rate limited by thiophene
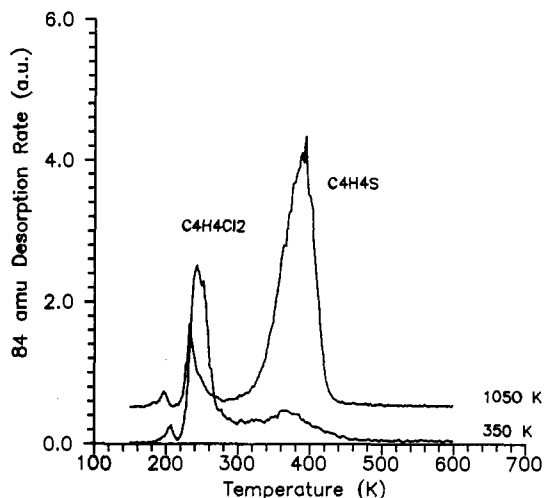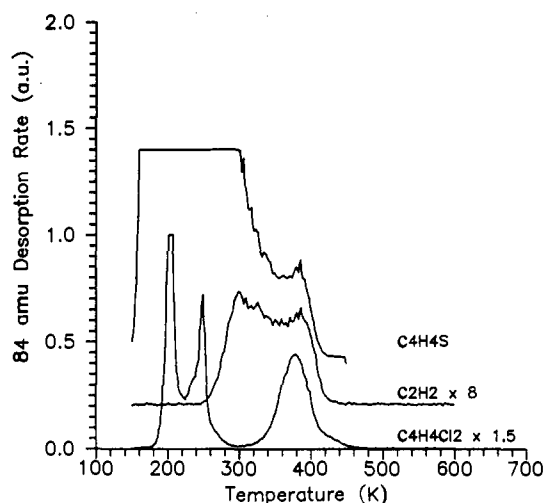
desorption kinetics. The assumption implicit in this argument is that the thiophene desorbing from the surface in this high-temperature range has not adsorbed dissociatively on the surface and is not the product of some recombination reaction of fragments produced during thiophene adsorption.

4. Discussion

4.1. Thiophene Synthesis Mechanism. The original work on acetylene cyclotrimerization to benzene demonstrated quite clearly that the reaction can occur via dimerization of acetylene to some C$_4$H$_4$ intermediate followed by cyclization of that intermediate with acetylene to yield benzene.[6,7] This sequential mechanism has been proposed over one involving a concerted three-body cyclization. Comparison of desorption kinetics following benzene adsorption and acetylene cyclotrimerization indicates that the appearance of benzene in the gas phase following cyclotrimerization is limited by benzene desorption kinetics.[6]

The chemistry described in this paper provides support for the sequential mechanism in the heterocyclization reaction producing thiophene. This comes initially from our observation of a reaction between adsorbed C$_4$H$_4$Cl$_2$ and sulfur which also yields thiophene. In addition, the fact that we have the heteroatom as the second reactant provides an additional degree of freedom with which to study these cyclization reactions. We have been able to examine

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their sensitivity to both sulfur coverage and the temperature at which the sulfur overlayers have been produced. Thiophene synthesis from both acetylene and from $C_4H_4Cl_2$ will occur only at sulfur coverages approaching saturation. Furthermore, both reactions exhibit the same dependence on the temperature at which the sulfur overlayer has been produced on the Pd(111) surface, occuring predominantly on the overlayers produced at high temperatures. These observations point toward a sequential mechanism for the heterocyclization reaction which is initiated by acetylene dimerization to a C_4H_4 intermediate which then cyclizes with sulfur to yield thiophene. Our comparison of thiophene desorption following acetylene, $C_4H_4Cl_2$, and C_4H_4S adsorption indicates that the thiophene is resident on the surface. As in the case of the cyclotrimerization reaction the appearance of the product in the gas phase is rate limited by the desorption step. This of course makes it impossible to determine which step of the reaction is in fact being influenced by the variations in sulfur coverage or the variations in the surface that are introduced by annealing.

Thiophene desorption resulting from acetylene heterocyclization occurs in the temperature range 280–420 K. The range over which thiophene desorption occurs suggests a great deal of heterogeneity in the surface and in the heats of adsorption of thiophene at different sites on this surface. In related work it has been possible to show that the sites at which these reactions are occurring are defects in the sulfur overlayer.[31,32] The primary difference between the heterocyclization of C_2H_2 and $C_4H_4Cl_2$ is that in the latter case the desorption of thiophene occurs over a narrower temperature range (360–420 K). The source of this difference is unclear; however, one possibility is that $C_4H_4Cl_2$ cannot dissociate at those sites at which thiophene would adsorb with a low heat of adsorption and hence desorb at low temperatures ($T < 360$ K).

At this point it is reasonable to discuss the nature of the species on the surface. Acetylene adsorption on the clean Pd(111) surface is quite well understood.[33,34] The molecule is bound in a di-σ/π configuration and is rehybridized upon adsorption. Although there has been no characterization of the molecule on the sulfided surface it is worth noting that the cyclization reactions occur on both surfaces. Although only benzene is observed on the clean surface, both benzene and thiophene are produced on the sulfided surface. Furthermore, it is apparent that both cyclotrimerization on the clean surface and heterocyclization on the sulfided surface are occurring by the same mechanism. As a result we suggest that the acetylenic species which initiates both reactions is identical.

The C_4H_4 intermediate produced from either C_2H_2 dimerization or dissociation of C–Cl bonds in $C_4H_4Cl_2$ will react with acetylene on the clean surface to yield benzene or sulfur on the sulfided surface to yield thiophene. The C_4H_4 species produced from acetylene must be present in only low concentrations or in transient form since it has never been isolated in studies of acetylene chemistry on the clean Pd(111) surface.[35] This species has, however, been isolated in high coverage during the decomposition of $C_4H_4Cl_2$ on the clean Pd(111) surface.[16] The assignment of the HREELS vibrational spectrum indicated that the species formed was a metallapentacycle with its ring plane tilted close to parallel with the surface. It should be noted that it is probably very difficult to discriminate this species from a cyclobutene species in which Pd atoms have been substituted for Cl atoms. Discrimination between the metallacycle and the cyclobutene with the HREELS spectrum was based on the absence of paraffinic CH stretching modes that exist in cyclobutene but which either do not appear in the spectrum of the C_4H_4 intermediate or cannot be resolved from the olefinic CH stretch. The intermediates isolated in studies of inorganic analogues of these cyclization reactions have been metallacycles. This is certainly true of the

heteroatom-cyclization chemistry in which rhodium–metallapentacycles react with sulfur to form thiophenes.[21,22]

The kinetics of thiophene desorption following heterocyclization are somewhat complicated. Desorption occurs over a broad temperature range with a peak shape that is clearly not that of a pure first order process. Using the Redhead equations for first-order desorption one finds that the heat of adsorption ranges from 18 to 24 kcal/mol.[36] One explanation for the peak width is that there is strong adsorbate–adsorbate repulsion which decreases the heat of adsorption at high coverage. This does not seem likely in this case given the relatively low coverages of thiophene that are desorbing and the fact that the desorption temperature range is independent of the coverage as seen in Figure 2. The width of the peak can also be indicative of surface heterogeneity, i.e. a distribution of sites at which thiophene is adsorbed with different heats of adsorption. Given the observation that desorption appears to occur over the same temperature range at both low and high thiophene coverages this seems to be most reasonable.

4.2. Catalyst Regeneration. One of the important aspects of the chemistry described in this work is that it represents a route to the removal of sulfur from metal surfaces. This is a necessary step in the regeneration of catalytic surfaces that have been deactivated by sulfur contamination. In general the high heat of adsorption of sulfur on metal surfaces makes this a difficult task requiring high temperatures. Classical approaches to the regeneration of contaminated surfaces include either calcination to remove sulfur as SO_2 followed by catalyst reduction or direct reduction of the catalyst in H_2 to remove sulfur as H_2S.[24,25] These attempts have been made over wide ranges of temperatures and pressures although for the most part successful attempts have required temperatures in the range 700–1100 K. The catalyst reduction treatments following calcination also require high temperatures which in the case of highly dispersed catalysts runs the risk of sintering. The formation of thiophene from acetylene and adsorbed sulfur is rate limited by thiophene desorption and occurs at comparatively low temperature (280–420 K). The only other reaction of a similar nature that we are aware of is one in which methanethiol and propanethiol have been found to desorb from the sulfided Pt(111) surface at 900 K following butadiene and hydrogen adsorption.[26]

Although in a single pass of acetylene adsorption followed by thiophene desorption we observe the removal of only a small fraction of the sulfur adlayer (~0.1%) in the presence of high pressures (1 Torr) of acetylene and continuous turnover of the acetylene monolayer, the complete abstraction of the sulfur monolayer would require only fractions of a second. The limitation of the reaction as performed under the conditions used in this work is that sulfur is only removed from the surface at coverages above some critical value near saturation. The barrier to reduction of surface sulfur to less than this critical coverage is not known. One possibility is that at high coverages the adsorbate–adsorbate interactions are sufficiently great that they reduce the heat of adsorption of sulfur to a point that the reaction becomes exothermic. If such is the case then performing the reaction at high pressures of acetylene may serve to drive the reaction further toward completion. On the other hand reduction of the surface sulfur coverage to less than the critical value may result in the opening of alternate reaction channels for acetylene on the exposed Pd surface in which case it may be impossible to reduce the sulfur coverage on this surface beyond this point.

5. Conclusions

The cyclization of acetylene with sulfur on the Pd(111) surface has been observed to produce thiophene in the gas phase. We have also shown that thiophene is produced from the adsorption of cis-3,4-dichlorocyclobutene on the sulfided surface. Both reactions are sensitive to the surface sulfur coverage, only occurring at coverages near saturation, and to the temperature at which the sulfur overlayer on the surface has been produced. The reaction

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occurs with greatest yield on the high-temperature sulfur phase. The fact that both reactions exhibit the same sensitivity to these surface characteristics suggests that the heterocyclization of acetylene is initiated by dimerization to form a C_4H_4 intermediate which then cyclizes with sulfur. Thiophene then desorbs from the surface in the temperature range 280–420 K. This surface chemistry offers a low-temperature route to the reduction of high surface sulfur coverages on the Pd(111) surface. The nature of the barrier to complete removal of surface sulfur is unknown; however, it is possible that at high pressures one might use this route to achieve complete regeneration of sulfur poisoned catalysts.

Face-Specific Interactions of Anionic Sulfur Donors with Oriented Crystals of (0001) CdX (X = Se, S) and Correlation with Electrochemical Properties

James J. Hickman and Mark S. Wrighton*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received September 17, 1990

Abstract: Oriented (0001) CdX (X = S, Se) crystals selectively adsorb $MoS_4{}^{2-}$ or $Et_2NCS_2{}^-$ onto the Cd-rich faces. Binding of the anions is effected by dipping the etched CdX crystals into CH_3CN containing 20 mM $[Et_4N]_2MoS_4$ or $Na[Et_2NCS_2]$. Removal of the crystal from the solution followed by rinsing with CH_3CN leaves $MoS_4{}^{2-}$ or $Et_2NCS_2{}^-$ on the Cd-rich, but not X-rich, face of the crystal as detected by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The specificity for Cd-face vs X-face binding is typically >5:1 as determined by XPS and AES data for both faces of the same crystal. S element maps for the $MoS_4{}^{2-}$-modified, Cd face of CdSe crystals reveal non-uniform binding of $MoS_4{}^{2-}$. There is a correlation of the regions of $MoS_4{}^{2-}$ binding with the crystal planes revealed in the pretreatment/etch procedure. Studies of interfacial capacitance of CdX/electrolyte systems show strong interaction of $MoS_4{}^{2-}$ selectively with the Cd-rich face, based on the relative flat-band shifts for the Cd- and X-rich faces when exposed to 10^{-2} M $MoS_4{}^{2-}$. However, repeated etching of the X-rich face with concentrated HCl reduces the degree of selectivity. The face-selective interaction of CdX with $Et_2NCS_2{}^-$ is also found from measures of the XPS and the photocurrent–voltage curves for the Cd- and S-rich faces. The binding sites for the anionic S donors are proposed to be exposed Cd^{2+} centers, but the etching of the (0001) surfaces prior to reaction exposes planes other than the Cd- or S-rich (0001) planes.

We wish to report that anionic S-containing species ($MoS_4{}^{2-}$ and $Et_2NCS_2{}^-$) adsorb selectively on the etched Cd-rich faces of (0001) oriented single crystals of CdX (X = S, Se) and that the electrochemical properties of these crystals in solutions containing the adsorbate are directly related to the adsorption. We have used X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), differential capacitance, and photoelectrochemistry to demonstrate the face selectivity of adsorption of anionic S-containing species on CdX. Our work extends previous studies on the interaction of anionic S-donors such as dithiocarbamates,[1] thiolates,[2-4] and polysulfides[5-7] on the Cd-rich face of (0001) CdX crystals. Such studies reveal that anionic S donors can strongly and favorably influence the CdX/electrolyte interface energetics to give highly efficient photoelectrochemical devices.[1-3,5-7] It has also been reported that amines interact with the Cd-rich face, and such interactions can be exploited in sensor devices.[8]

Our new study was undertaken to better understand the role of crystal orientation in determining the degree of interaction of CdX with anionic S donors. One would expect different chemistry at the two faces of (0001) CdX, based on differences in structure and composition. Significant differences have been reported earlier.[9] In particular, differential capacitance measurements have shown that the Cd, but not S, face of (0001) CdS interacts strongly with S^{2-}.[10] More recently it has been shown that Fe-$(CN)_6{}^{3-/4-}$ interacts more favorably with the Cd-rich face of CdX.[11] Also, it has been suggested that an ion-specific electrode could be based on the selective interaction of SH^- with the Cd

face and Cd^{2+} with the S face of CdS.[12]

It is important to correlate interaction of anionic S-donor species with the electrochemical behavior of the crystals. A strong in-

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*Address correspondence to this author.