

Selective Hydrogenation of Acetylene over Palladium in Ultra High Vacuum

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Under ultra-high-vacuum conditions, precoverage of a palladium(111) surface with hydrogen does not affect either the kinetics or the extent of acetylene uptake at 175 K. The subsequent reactive behavior of the system is however radically altered. Benzene formation is strongly suppressed, the transformation of adsorbed acetylene to another species (β -phase) is enhanced, and the yield of ethylene is increased. Ultraviolet photoelectron spectroscopy (UPS) observations and coverage measurements suggest that the β phase consists at least partly of vinylidene, although some ethylidyne may also be present. Experiments with deuterium suggest that vinylidene may be the precursor to ethylene formation; flat-lying acetylene is responsible for benzene production.

Introduction

Palladium provides a particularly suitable model substrate for the study of hydrocarbon hydrogenation over group VIII (groups 8–10)²⁷ metals since surface reactions under ultra-high-vacuum (UHV) conditions appear to mimic those that occur with high reactant pressures. Thus the desorption products arising from an acetylene-covered palladium surface include ethylene;^{1,2} this behavior does not appear to be typical of other group VIII (groups 8–10) metals.³ Palladium, therefore, offers the opportunity to study in detail and under UHV conditions reaction pathways and reaction intermediates which may be of significance at higher pressures. This paper presents UPS and thermal desorption spectroscopic (TDS) data with which the structural and kinetic properties of acetylene adsorbed onto a hydrogen pre-dosed Pd(111) surface are examined.

It was shown in previous publications^{1,2} that acetylene adsorbs on Pd(111) at low temperature (~ 150 K) with its C–C axis parallel to the crystal surface. On warming, two alternative reaction pathways to gaseous products were identified: benzene formation and a competing self-hydrogenation reaction to form ethylene.^{1,2} This unusual formation of benzene on palladium(111) has been independently confirmed^{4,5} and although HREELS studies of acetylene on nickel do suggest that initial formation of benzene occurs,⁶ subsequent desorption is not possible. The hydrocarbon fragment formed by warming the acetylene layer on Pd(111) to room temperature was identified on the basis of UPS and coverage data as vinylidene,² although HREELS data suggest that ethylidyne coexists with vinylidene at this surface.^{7,8}

Experimental Section

The vacuum chambers, sample cleaning methods, and experimental procedures have been described in detail in earlier publications.^{2,9} Thermal desorption experiments were performed using an apparatus equipped with a capillary array dosing source which ensured a uniform gas exposure at the crystal without excessive contamination of the chamber. This source also allowed acetylene adsorption kinetics to be rapidly and conveniently monitored by measuring the time dependence of the scattered gas signal due to acetylene.² These experiments were performed as follows. The rise in chamber pressure due to the gas leaking in through the molecular beam source was monitored by using the mass spectrometer with the crystal out-of-beam. The specimen was then rapidly moved to intercept the beam causing the chamber pressure to drop sharply. The pressure slowly rose to its former value as the surface saturated, resulting in a pressure vs. time curve of the

type shown in Figure 1. This method of measuring adsorption kinetics yields data that agree very well with those obtained by more conventional methods.² The second chamber, a VG Scientific ADES 400 angle-resolving XP/UP spectrometer was used for the photoelectron spectroscopy measurements. The hydrogen and deuterium were of spectroscopic grade and were used without any further purification. Acetylene was purified using six bulb-to-bulb distillations to remove any acetone or benzene impurities. No impurities in the final product were observable mass spectroscopically.

Results

Experiments were performed in all cases by pre-dosing the surface with hydrogen (or deuterium) followed by exposure to acetylene. Figure 1 shows the pressure vs. time curve for acetylene dosing on a Pd(111) surface pre-exposed to 2 langmuirs of deuterium at 175 K; the capillary array dosing source was used for these measurements. The hydrogen coverage at this stage (referred to the number density of Pd atoms) would be $\theta_{\text{H}} \sim 0.4$. The curve in Figure 1 is identical with the trace obtained for acetylene adsorption onto a *clean* Pd(111) surface,² indicating that the adsorption kinetics and saturation coverage of acetylene appear to be unaffected by hydrogen pre-dosing. In particular, the initial sticking probability and saturation coverage of acetylene remain unchanged at ~ 1.0 and ~ 0.46 , respectively.² Experiments performed on surfaces with various hydrogen exposures showed that acetylene adsorption was unaffected at all hydrogen pre-coverages.

The He I UP difference spectra derived from a surface initially at 175 K and dosed sequentially with hydrogen (10 langmuirs) and acetylene (2.6 langmuirs $\theta_{\text{C}_2\text{H}_2} = 1/3$) are shown in Figure 2 as a function of subsequent heating in the interval 189–420 K. These difference spectra were obtained by heating the pre-covered sample to the desired temperature for 10 s, cooling, and then

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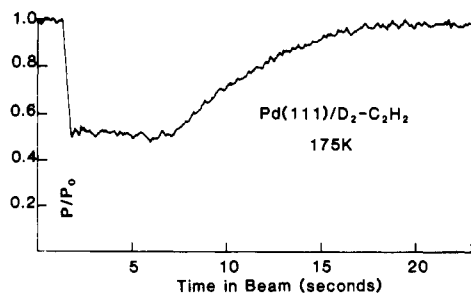


Figure 1. Pressure vs. time trace using the capillary array source for the adsorption of acetylene onto a Pd(111) surface pre-dosed with 2 langmuirs of D_2 at 175 K.

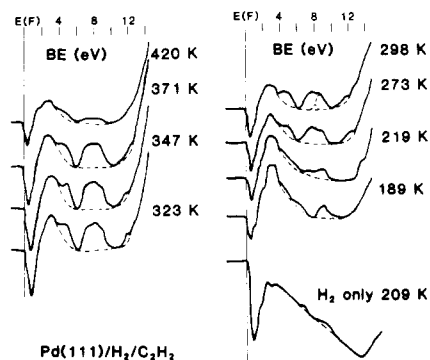


Figure 2. He I UP difference spectra for hydrogen + acetylene on a Pd(111) sample as a function of temperature ($\psi = 50^\circ$, $\theta = 40^\circ$).

recording the spectrum. They were derived by subtracting Pd(111) + H_2 spectra from Pd(111) + H_2 + C_2H_2 spectra obtained at corresponding temperatures; thus they exhibit only acetylene-derived features. A difference spectrum for H_2 alone at 209 K is shown for comparison purposes. The photon incidence angle (ψ) and photoelectron emission angle (θ) were 50° and 40° , respectively, relative to the surface normal. This configuration was chosen so that no transitions would be symmetry forbidden. A single feature at 9.0 ± 0.1 eV below the Fermi edge is visible up to a temperature of 189 K. On warming, more intense features appear with peaks at 4.9, 7.4, 8.7, 11.8 (all ± 0.2) eV below the Fermi edge. The peaks at 8.7 and 7.4 eV are not well resolved, and the estimated components are shown in the 298 K spectrum. These features grow with increasing temperature, reaching a maximum intensity at 323 K; subsequent warming to 371 K caused little change in the spectra. However, all features diminish considerably in intensity on warming to 420 K.

Thermal desorption spectra were recorded at 2, 26, 28, 30, and 78 amu after dosing the surface with 10 langmuirs of H_2 + 2.3 langmuirs of C_2H_2 at 175 K (Figure 3). The results are in general accord with the well-known propensity of Pd to act as an efficient selective hydrogenation catalyst. Thus there is no detectable yield of ethane (30 amu) and the major gaseous hydrocarbon product is ethylene (26, 28 amu). (The small peak at ~ 510 K in the 28 amu spectrum is due to impurity CO; the 26 amu signal is entirely due to the $C_2H_2^+$ fragment from $C_2H_4 - C_2H_2$ itself exhibits a completely different desorption spectrum.²) Notice also that benzene formation (78 amu) is strongly suppressed by the presence of coadsorbed hydrogen; this is an important reaction pathway when hydrogen pre-dosing is not carried out.² The H_2 spectrum exhibits three principal features: a broak peak at ~ 250 K, a sharp peak at ~ 450 K, and a broad band of desorption extending to higher temperatures. The 250 K peak is due to desorption of chemisorbed hydrogen, and the other features closely resemble the H_2 desorption spectra which result from the chemisorption of acetylene alone.²

An estimate of the apparent activation energy to the formation of gaseous ethylene may be made by considering only the leading edge region of the desorption trace. The validity of such an analysis rests on the assumption that the reactant concentrations remain effectively constant if a sufficiently small portion of the

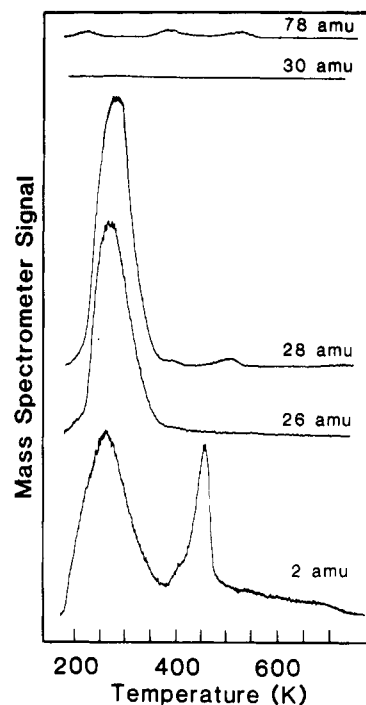


Figure 3. 2 amu (H_2), 26 amu (C_2H_2), 28 amu (C_2H_4), 30 amu (C_2H_6), and 78 amu (C_6H_6) desorption spectra obtained after exposure of a Pd(111) surface to H_2 (10 langmuirs) and C_2H_2 (2.3 langmuirs) at 175 K (heating rate 21 K s^{-1}).

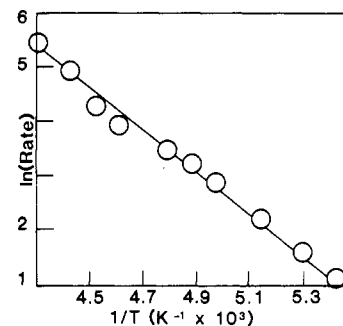


Figure 4. Leading edge Arrhenius plot for the reactive desorption of ethylene obtained from the data of Figure 3.

desorption sweep is considered. The gradient of a plot of \ln (desorption rate) vs. $1/T$ yields the activation energy directly, and deviation of this curve from linearity indicates eventual breakdown of the initial approximation. Figure 4 shows a leading edge Arrhenius plot for the appearance of ethylene in the gas phase and yields an activation energy of 31 ± 2 kJ/mol. Additional thermal desorption experiments with deuterium were performed by pre-dosing the surface with either 2 langmuirs or 10 langmuirs of D_2 at 175 K and then saturating with acetylene and taking spectra at 28, 29, 30, 31, and 32 amu. The results of these measurements are shown in Figure 5. Two-langmuir preexposure to deuterium results in the desorption of predominantly C_2H_4 and C_2H_3D accompanied by small amounts of ethylene- d_2 , $-d_3$, and $-d_4$; when the deuterium exposure is increased to 10 langmuirs, the 30 amu signal increases by a factor of 10, indicating substantial $C_2H_2D_2$ formation under these conditions. The peak temperature is the same for all the reactively formed deuterioethylenes. This implies that H (or D) transfer from the metal to the organic moiety is not the rate-determining step in the selective hydrogenation reaction.

Discussion

The low-temperature acetylene adsorption kinetics on Pd(111) are unaffected by deuterium pre-dosing (Figure 1). Thus acetylene adsorbs with an initial sticking probability of about unity via a mobile precursor state, reaching saturation at $\theta(C_2H_2) = 0.46$.²

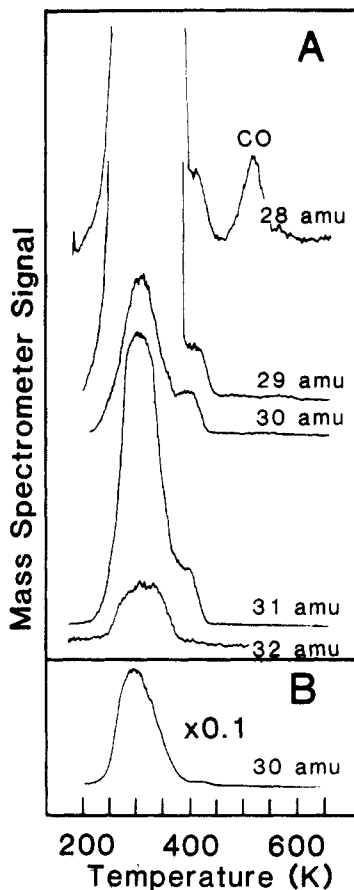


Figure 5. Thermal desorption spectra of deuterated ethylene after the exposure at 175 K to (A) 2 langmuirs of D_2 + saturation C_2H_2 . Relative desorption yields are 10, 10, 0.6, 1.2, and 0.3 at 28, 29, 30, 31, and 32 amu, respectively. (B) 10 langmuirs of D_2 + saturation C_2H_2 .

This may suggest that hydrogen and acetylene require different adsorption sites at low temperature. In this connection, it is worth noting that UPS results suggest that for Pd above 100 K hydrogen adsorbs below the first layer of metal atoms.¹⁰ The UP spectrum taken at 150 K (Figure 2) yields a major peak at ~ 9.0 eV below the Fermi edge at an identical position with that for emission from a low-temperature acetylene-derived phase on clean palladium-(111).² This peak was assigned to emission from the σ_{CCH} orbital of a *flat-lying acetylene molecule*, and in view of the similarity in adsorption kinetics and emission spectra in the two cases, it may be assigned to a similar species in the present case (denoted α -phase). Emission from the π and σ_s^* orbitals is not observed in this spectrum since the bands are obscured by the metal d-region and inelastic peaks respectively.

Warming the (H_2 + C_2H_2)-dosed surface desorbs H_2 in the range ~ 200 – 350 K in agreement with the reported desorption behavior of H_2 from clean Pd(111) following low-temperature adsorption.¹¹ The rate maximum for ethylene desorption occurs at ~ 270 K at which stage the UP data indicate that formation of a new hydrocarbon surface phase (denoted β -phase) is complete. This indicates that the β -phase participates directly in the selective hydrogenation. Note also that the apparent activation energy to desorption for the reactively formed ethylene (~ 31 kJ/mol) is quite distinct from that for the desorption of ethylene from a Pd(111) surface dosed with *ethylene* at low temperature (~ 54 kJ/mol²³). Evidently, the rate-limiting step in the present case is *not* the desorption of a *flat-lying* ethylenic species such as is formed by the low-temperature adsorption of ethylene itself.²³

Photoemission from the hydrocarbon β -phase maintains constant intensity up to ~ 370 K. At ~ 420 K the intensity is strongly

attenuated and this correlates with the appearance of the higher temperature peak in the H_2 desorption spectrum which may be ascribed to the decomposition of the β -phase.

Consider now the nature of the thermally activated surface hydrocarbon species that is characterized by emission peaks at 4.9, 7.4, 8.7 and 11.8 below E_F . An earlier UPS investigation of the adsorption of *acetylene* onto clean Pd(111) at room temperature² reported spectra exhibiting peaks at 4.6, 6.6, 7.9, and 11.1 (± 0.2 eV) below the Fermi edge. These were assigned to a vinylidene species partly because of the correspondence between the spacings of these peaks and those of gas-phase ethylene. While there is an overall shift of energies in the present case (possibly due to the preadsorbed hydrogen), the band spacings are sufficiently similar to suggest the same species is again present.

HREELS analysis of the room temperature *ethylene*-derived species on Pd(111)¹² showed this to be an ethylidyne hydrocarbon fragment since its vibrational frequencies were in good agreement with the infrared and Raman frequencies of a $(CO)_9Co_3CCH_3$ cluster compound.¹³ However, a UPS investigation by Lloyd and Netzer¹⁴ of the room temperature *ethylene*-derived species gave a spectrum with peaks at 4.8, 7.0, and 8.3 eV which the authors assigned to ethylidyne. Within experimental error, this agrees with the spectrum from *acetylene* on Pd(111) at room temperature.² Assuming that the ethylene/HREELS assignment is correct, there appear to be two possible explanations for this remarkable agreement. Either the room temperature acetylene-derived species is in fact an ethylidyne, or both ethylidyne and vinylidene species yield identical photoelectron spectra. Note however that Lloyd and Netzer did not see any peak beyond the 11-eV peak for ethylene on Pd(111) since only HeI radiation was used. Now in ethylene the σ_s^* ($2a_u$) to σ_{CH_2} ($1b_{3u}$) spacing is 3.2 eV, whereas in ethane the corresponding σ_s^* ($2a_u$) to e_{CH_3} ($1e_u$) spacing is 5.0 eV, and these values could be expected to be maintained in the vinylidene and ethylidyne spectra, respectively. The present observation of a 3.1-eV spacing thus tends to favor the former alternative.

A further piece of evidence in support of the vinylidene interpretation for $C_2H_2/Pd(111)/300$ K comes from the observed saturation coverages of hydrocarbon species on Pd and Pt at room temperature. For $C_2H_2/Pd(111)$, molecular beam, XPS, and LEED data give a fractional coverage at saturation of 1.0.² On the other hand the saturation coverage of ethylidyne on Pt(111) has been measured at 0.25.^{15–17} Although it has been suggested from XPS data that this value should really be 0.5,^{18,19} more recent observations using TDS, Auger spectroscopy, XPS, and ^{14}C radiotracer experiments²⁰ are all consistent with an ethylidyne saturation coverage on Pt of 0.25. Given the identical crystal structures and closely similar interatomic spacings of Pd and Pt, it seems reasonable to assume that the fractional coverage at saturation for ethylidyne on Pd(111) would also be ~ 0.25 . The value of ~ 1.0 found for Pd(111)/ C_2H_2 would therefore seem to rule out ethylidyne.

The net result of these arguments is to cast some doubt on the identification of the room temperature C_2H_2 or C_2H_4 species on Pd(111) as ethylidyne. It is unfortunate that HeI radiation was not used by Lloyd and Netzer in their Pd/ C_2H_4 work; this would have permitted observation of the σ_s^* orbital thereby enabling a more stringent comparison with our own Pd/ C_2H_2 results. Results obtained with dispersed metals do not appear to permit an unequivocal resolution of this ambiguity. Thus on the one hand

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TABLE I: Peak Positions and Spacings^a

	$\sigma_{\text{CH}_2}^*$	Δ	σ_{CC}	Δ	σ_{CH_2}	Δ	σ_{S}^*
C ₂ H ₂ /H ₂ /Pd(111) this work	4.9 ± 0.2	2.5 ± 0.4	7.4 ± 0.2	1.3 ± 0.4	8.7 ± 0.2	3.1 ± 0.4	11.8 ± 0.2
C ₂ H ₄ /Pd(111) ¹⁴	4.8	2.2	7.0	1.3	8.3		
C ₂ H ₂ /Pd(111) ²	4.6	2.0	6.6 ± 0.2	1.3	7.9 ± 0.2	3.2	11.1 ± 0.2

^aEnergies are in electronvolts measured with respect to the Fermi edge. Δ signifies the spacings (in eV) between peaks.

Beebe et al.²⁴ have used IR spectra to infer the formation of ethylidyne from acetylene on Al₂O₃-supported Pd. Conversely however, the NMR observations of Wang et al.²⁵ on Al₂O₃-supported Pt have been interpreted in favor of vinylidene formation. In any event, in the present case the evidence on balance seems to favor identification of a vinylidene-like species with the room temperature β -phase formed from acetylene on Pd(111).

For the H₂ + C₂H₂ mixed adsorption layer, peak positions and spacings are shown in Table I. These are in agreement with our earlier results for C₂H₂ alone, and in view of the preceding discussion, the spectroscopic data alone do not permit unambiguous assignment to either vinylidene or ethylidyne. An estimate of the saturation coverage of the hydrocarbon species does however provide some further insight. This may be carried out in two ways. A comparison of UPS peak intensities with those for the Pd/C₂H₂/300 K system at saturation coverage² yields a value of ~ 0.4 . This however does depend on the assumption of identical hydrocarbon species with identical photoionization cross sections in the two cases. A better approach is to measure the hydrocarbon loss in the present case when the system is warmed from 175 to 300 K and subtract this from the initial low-temperature saturation coverage. The molecular beam measurements show this latter quantity to be $\theta = 0.46$ (unaffected by the presence of hydrogen), and the TDS data show that hydrocarbon is lost predominantly by ethylene desorption. The reactively formed ethylene lost by this route in the interval 175–300 K can be estimated by comparison with the desorption spectrum from a surface saturated with ethylene at 175 K.²³ Such a comparison shows that in the present case ~ 0.02 of a monolayer of hydrocarbon is removed by ethylene desorption. This implies a hydrocarbon coverage of ~ 0.44 in the 300 K adsorption layer, in good agreement with the estimate from UPS intensities. The figure of ~ 0.44 appears to rule out the possibility that the hydrocarbon phase consists entirely of ethylidyne ($\theta_{\text{max}} = 0.25$). It would however be consistent with the presence of vinylidene or a mixture of vinylidene and ethylidyne.

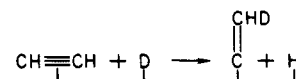
A revealing comparison may be made of the H₂ desorption spectra obtained here following 175 K adsorption of (H₂ + C₂H₂) with those obtained for pure C₂H₂ and pure C₂H₄ under the same conditions. Ethylene alone gives a hydrogen desorption peak at ~ 375 K²¹—presumably due to ethylidyne decomposition. Under identical conditions, acetylene yields a hydrogen peak at 450 K.² In the present case, the H₂ peak also occurs at 450 K, again tending to support the view that ethylidyne is not the dominant surface species formed by acetylene. (The occurrence of a small amount of ethylidyne decomposition cannot be ruled out because the corresponding H₂ peak at 375 K would be obscured by the trailing edge of the peak due to desorption of chemisorbed hydrogen). Preadsorbed hydrogen appears not to perturb the adsorption kinetics of acetylene: the behavior on clean and hydrogen-precovered surfaces is essentially identical. Therefore the possibility exists that acetylene chemisorption is accompanied by hydrogen displacement; such an effect would lead to significant diminution of the H₂ desorption yield in the 250 K peak (Figure 3) from an H₂ predosed, acetylene-saturated surface. In this particular case, because $\theta_{\text{H}} = 1$ and $\theta_{\text{C}_2\text{H}_2} = 1/3$,² the relative yields of preadsorbed hydrogen (250 K peak) and acetylene-derived hydrogen (450 K and above) should be in the ratio 1.5:1 if no

hydrogen displacement occurred. The observed value of $\sim 1.33:1.00$ corresponding sufficiently closely as to indicate displacement of preadsorbed hydrogen is not an important process.

The selectivity of the hydrogenation reaction under UHV conditions appears to mimic that at higher pressures: ethylene rather than ethane is produced. This implies that ethylidyne, if present, does not undergo hydrogenation to ethane. A similar conclusion was reached in the case of Pt²² where ethylidyne undergoes H/D exchange but not hydrogenation. Recently, it has been shown that ethylidyne does not participate directly in the high-pressure hydrogenation of ethylene over Pt.²⁶

The almost complete suppression of benzene formation by preadsorbed hydrogen is also entirely consistent with an enhanced acetylene \rightarrow vinylidene transformation. Thermal desorption results from a surface dosed with acetylene at low-temperature strongly suggest that the α -phase (i.e., flat-lying acetylene) is a precursor to benzene formation.^{1,2} This interpretation is consistent with the present data; an enhanced acetylene \rightarrow vinylidene transformation in the presence of preadsorbed hydrogen implies a lower surface concentration of flat-lying acetylene and therefore a diminution in benzene yield.

It therefore seems clear that preadsorbed hydrogen assists the acetylene \rightarrow vinylidene transformation at the expense of benzene formation, so that all the flat-lying acetylene converts to vinylidene/ethylidyne on warming to 270 K in the presence of hydrogen. This may imply that preadsorbed hydrogen can participate directly in H migration to the β -carbon. A possible route for this process could be



Although the apparent activation energy of acetylene hydrogenation (Figure 4, 31 ± 2 kJ/mol) is of the same order as that for the high-pressure reaction (46 kJ/mol, ref 23), no strong conclusion can be drawn about similarities between reaction mechanism in the two cases. In principle, it is possible for both flat-lying acetylene and upright vinylidene to undergo partial hydrogenation to C₂H₄. In the presence of preadsorbed deuterium, the former species might be expected to yield 1,2-ethylene-d₂ at all deuterium precoverages (assuming that vinylidene does not undergo H–D exchange). However, any such H–D exchange would lead to ethylene-d_n with $n > 2$. This is contrary to present observations (Figure 5). Furthermore, the UPS results show that acetylene rearrangement is underway by 220 K, and is complete by about 270 K while the ethylene desorption peak occurs at about 270 K. This supports the view that under UHV conditions it is

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(27) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

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the β -phase which is the precursor to ethylene formation.

Conclusion

The adsorption kinetics and UP spectroscopic behavior of acetylene on a hydrogen-predosed surface at 175 K show that the α -phase is the same as that resulting from the low-temperature adsorption of acetylene alone, that is, an essentially flat-lying acetylenic species with the C-C axis parallel to the metal surface. On raising the temperature, the principal desorption product is ethylene. Benzene formation is markedly suppressed compared to a hydrogen-free surface, whereas the proportion of acetylene transforming to vinylidene/ethylidyne is increased. These observations provide corroborating evidence that the precursor to

benzene formation is indeed the flat-lying acetylene. Warming the surface to about 270 K forms a β -phase which UPS, TD, and coverage data suggest consists primarily of vinylidene; however, the presence of some ethylidyne cannot be excluded. Formation of the β -phase is enhanced by preadsorbed hydrogen or deuterium. In the latter case, the isotope distribution in the product suggests that under UHV conditions upright vinylidene undergoes partial hydrogenation to ethylene.

Acknowledgment. We thank Johnson Matthey Ltd. for the loan of precious metals.

Registry No. Pd, 7440-05-3; acetylene, 74-86-2; benzene, 71-43-2; ethylene, 74-85-1.

Trimethylgallium Adsorbed on Silica and Its Reaction with Phosphine, Arsine, and Hydrogen Chloride: An Infrared and Raman Study

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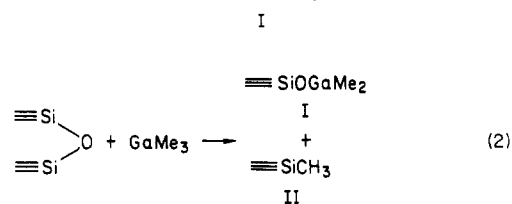
The reaction of trimethylgallium, GaMe₃, with silica has been studied by using infrared (4000–500 cm⁻¹) and Raman (3500–100 cm⁻¹) spectroscopies. Regardless of the temperature used to activate the silica under vacuum the major reaction is with the surface hydroxyl groups: $\equiv\text{SiOH} + \text{GaMe}_3 \rightarrow \equiv\text{SiOGaMe}_2$ (I) + CH₄. For silica activated at greater than 400 °C, reactive siloxane bridges also react to yield I and $\equiv\text{SiCH}_3$ (II). Almost all vibrational modes of I have been observed by using the two spectroscopic techniques. At 20 °C, PH₃ and AsH₃ coordinate to the gallium atom of I and there is also a small degree of decomposition of this complex since traces of $\equiv\text{SiOH}$ and CH₄ are generated. With increasing temperature this decomposition is accelerated until, near 250 °C, GaP and GaAs are formed. Species I reacts within 1 min at 20 °C with gaseous HCl to eliminate one methyl group as CH₄, and over the next 24 h the second methyl group is also converted to methane. The mechanism is complex since $\equiv\text{SiOH}$ groups are also created thus indicating that HCl can cleave the SiOGa bond, and spectroscopic evidence shows that monomeric GaCl₃ and $\equiv\text{SiOGaCl}_2$ may constitute the final product.

A variety of chlorine- and methyl-containing hydrogen sequestering agents such as SiCl₄Me_{4-x}, GeCl₄Me_{4-x} [*x* = 1–4, Me = CH₃], Al₂Me₆, BCl₃, TiCl₄, and Me₃SiNSiMe₃ [hexamethyldisilazane, HMDS] have been used to probe the nature of the surface hydroxyl groups on silica, or to chemically modify the silica surface for other purposes.^{1–6} Transmission infrared spectroscopy has been the most commonly used technique in these studies in spite of the fact that self-supporting disks are only transparent in the mid-infrared above about 1300 cm⁻¹, i.e., in the SiOH stretching (3750–3300 cm⁻¹), CH₃ stretching (3000–2800 cm⁻¹), and CH₃ deformation (1400 cm⁻¹) regions. However, we have shown that Raman spectroscopy can be used to obtain low-frequency spectral data^{1,7} and very recently we have shown that complementary low-frequency data can also be obtained using thin film infrared transmission spectroscopy.⁶

This paper is concerned with the use of all three of the above techniques to study the adsorption of trimethylgallium, GaMe₃, on silica, and its subsequent reactivity with a variety of molecules. Trimethylgallium, unlike the alkyl silicon and germanium derivatives, is extremely reactive at ambient temperatures, and, unlike its aluminum counterpart, is a monomer at this temperature or higher. Gallium anchored to some oxides is reported to have unusual catalytic activity^{8,9} and since GaMe₃ is widely used to produce GaP and GaAs semiconducting devices,^{10–12} we have also studied the reactivity of the GaMe₃ modified surface with PH₃ and AsH₃.

To our knowledge the only other report of the reaction of GaMe₃ with silica is that of Tubis et al.⁸ They found that after reaction, new IR bands were observed at 3012 (sharp), 2960

(broad), and 2915 (weak) cm⁻¹ which were assigned to species (I and II) from the reactions 1 and 2. Since after admission of



air, and evacuation, the 3012-cm⁻¹ band disappeared whereas the others remained, this band was assigned to a Ga-CH₃ vibration

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