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On the Mechanism for the Conversion of Ethylene to Ethylidyne on Metal Surfaces: Vinyl Halides on Pt(111)

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Abstract: The thermal chemistry of vinyl halides adsorbed on Pt(111) surfaces was studied by using thermal programmed desorption (TPD) and reflection-absorption infrared (RAIRS) spectroscopies. In the case of vinyl iodide some molecular desorption occurs at high coverages around 130 (multilayer) and 150 K (monolayer), and the remaining vinyl iodide then decomposes via an initial scission of the C–I bond, a step that presumably leads to the formation of surface vinyl groups. RAIRS experiments indicate that the subsequent conversion of this latter species may involve the formation of several intermediates, starting with a mixture of μ_3-η^2-vinylidene and μ_3-η^2-acetylene (both moieties coordinated to three metal atoms via both σ and π bonds). The vinylidene disappears around 170 K, while the acetylene subsists to higher temperatures, but above 200 K no infrared signal can be seen in the IR experiments, a fact that we interpret as the result of the formation of a new flat-lying species on the surface, possibly π-coordinated ethylene. Finally, heating above 300 K leads to the formation of ethylidyne. Based on these studies we conclude that since adsorbed vinyl groups eventually convert into ethylidyne but only by going through a series of intermediates that possibly includes ethylene, it is unlikely for the conversion of ethylene to ethylidyne to involve vinyl intermediates.

1. Introduction

In spite of the numerous studies on the thermal reactivity of olefins on transition-metal surfaces carried out to date, the details of the reactions involved in those systems remain somewhat unknown.[1] It is well-known that chemisorbed ethylene converts into ethylidyne around room temperature on a number of surfaces (including Pt(111),[2,3] Pt(100),[4,5] Rh(111),[6] Rh(100),[7] Pd(111),[8] Ru(100),[9] Ir(111),[10] and supported platinum,[11] palladium,[12] and nickel[13] catalysts), but the mechanism for such reaction is still unclear.[7,14–17] A family of possible intermediates has been suggested, including ethyl (CH_2CH_3),[7] vinyl ($CHCH_2$),[18] ethylidene ($CHCH_3$),[19] and/or vinylidene (CCH_2).[20] In order to narrow down those options, we recently carried out thermal desorption (TPD) experiments using $CHD{=}CD_2$ in which we made use of an observed kinetic isotope effect[21,22] to differentiate between steps involving C–H and C–D bonds.[18] It was concluded then that the limiting step for ethylene conversion involves the hydrogen atom that desorbs in the first TPD feature (around 300 K), a result that rules out any simple mechanism involving ethyl or ethylidene intermediates and supports the idea of the formation of vinyl moieties instead.[18]

Studies on the thermal chemistry of vinyl halides on Pt(111) surfaces were performed here in order to test further the hypothesis postulated above. Because of the ease with which carbon–halogen bonds break, halogen substituted hydrocarbons are potential good precursors for the preparation of surface carbon containing groups;[23] recent studies have shown that vinyl moieties can indeed be prepared by thermally activating adsorbed vinyl iodide.[24] The experiments reported here indicate, however, that the conversion of those vinyl groups to ethylidyne involves at least three additional intermediates, namely, vinylidene, acetylene, and ethylene. The likelihood of vinyl moieties actually been intermediates in the conversion of ethylene to ethylidyne is discussed in view of these new results.

2. Experimental Section

The experiments reported here were carried out in an ultrahigh vacuum (UHV) stainless steel chamber described in part in previous publications.[25,26] Briefly, the apparatus is pumped to a base pressure of less than 1×10^{-10} Torr and is equipped with instrumentation for thermal programmed desorption (TPD), low-energy electron diffraction (LEED), Auger electron (AES), and reflection-absorption infrared (RAIRS) spectroscopies.

Thermal desorption spectra were taken with a differentially pumped mass spectrometer located directly above the sample. A stainless steel tube with a 5-mm diameter orifice was placed within 2 mm of the crystal front face in order to enhance the detection of molecules desorbing from that surface and to discriminate against background gases. Signals for

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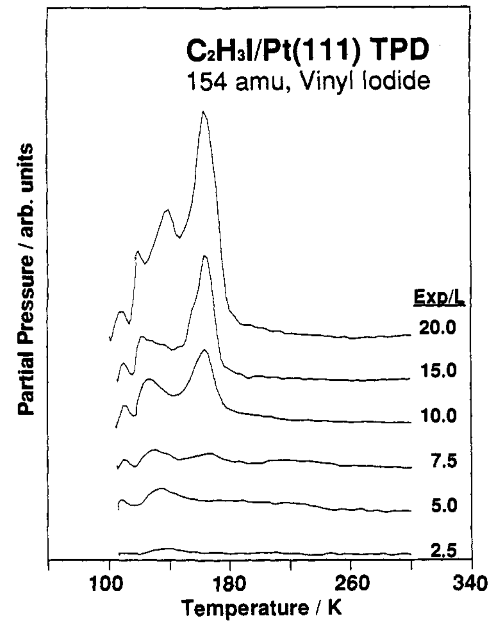

Figure 1. Molecular TPD spectra for vinyl iodide ($CH_2=CHI$) adsorbed on a Pt(111) surface at 90 K as a function of initial exposure. The heating rate in these experiments was about 10 K/s.

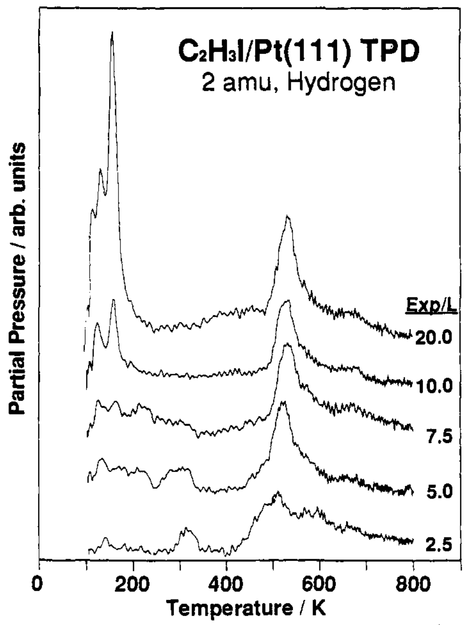

Figure 2. Hydrogen TPD spectra for vinyl iodide adsorbed on Pt(111) as a function of initial exposure.

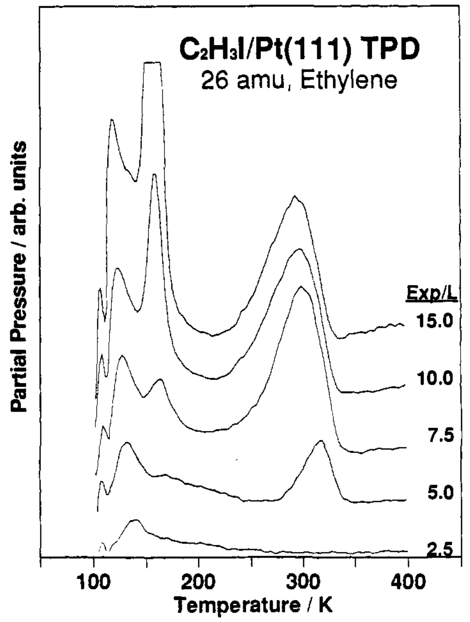

Figure 3. Ethylene (26 amu) TPD spectra for vinyl iodide adsorbed on Pt(111) as a function of initial exposure.

up to ten masses were taken simultaneously in a single TPD experiment by using an interfaced computer. A heating rate of about 10 K/s was used.

Reflection-absorption infrared spectroscopy experiments were done by taking the IR beam from a Mattson-Sirius 100 FT-IR spectrometer and focussing it through a sodium chloride window onto the sample (under vacuum) at an incident angle of 80 ± 3°, passing it after reflection sequentially through a second sodium chloride window and a polarizer, and collecting it on a mercury–cadmium–telluride (MCT) detector.[25–27] The spectra shown here were taken with 4-cm^{-1} resolution and ratioed against background spectra for a clean surface taken immediately before the experiment. Each spectrum was the result of a 1000 scan average (300 s acquisition time).

The platinum single crystal was cut and polished in the (111) orientation by using standard procedures and mounted in a manipulator so it could be cooled to liquid nitrogen temperatures and resistively heated to above 1500 K. The crystal temperature was monitored with a chromel-alumel thermocouple spot-welded onto the edge of the crystal. Cleaning of the platinum surface by cycles of oxygen treatment at 1000 K, ion sputtering, and annealing to 1300 K was done prior to each experiment until no impurities were detected by AES. Vinyl iodide (>85%) and vinyl bromide (98%) were obtained from Lancaster and Aldrich, respectively, purified by following several freeze–pump–thaw cycles before leaking them into the vacuum chamber, and checked periodically by mass spectrometry. All crystal dosing was done by backfilling of the vacuum chamber. Exposures are reported in Langmuirs (1 L = 10^{-6} Torr·s); the pressures are uncorrected for differences in ion gauge sensitivity.

3. Results

Only hydrogen, ethylene, and molecular vinyl iodide were seen to desorb from vinyl iodide adsorbed on Pt(111); other products looked for and not detected include methane, ethane, butane, butene, butadiene, and benzene. The coverage dependence of the TPD spectra for this system is reported in Figures 1–3. Vinyl iodide molecular desorption starts above 5 L with a peak that grows about 160 K and that is associated with desorption from the first monolayer (Figure 1). That peak saturates around 15 L, after which a second feature develops below 140 K due to multilayer condensation. The small features below 130 K are due to desorption from the sample holder.

Figure 2 displays traces for hydrogen desorption from the same system. Two features are seen in the spectra for the low doses (below 3 L), one sharp small peak around 320 K, and a second broader and complex one starting around 400 K and having two maxima about 520 and 590 K. Since hydrogen desorption from adsorbed hydrogen on a clean Pt(111) surface takes place around 380 K, the low-temperature feature observed here suggests that some vinyl iodide decomposition occurs at quite low temperatures in the low coverage limit, probably around 300 K or below. As the vinyl iodide exposure is increased, however, the 320 K feature disappears, and hydrogen desorption is only observed above 500 K: TPD spectra from saturation coverages display one main peak about 540 K and a shoulder around 670 K. The peaks seen at low temperatures (below 200 K) in all spectra are due to cracking of the vinyl iodide that desorb molecularly in the mass spectrometer.

Ethylene desorption was followed by simultaneously detecting the signals for 26, 27, and 28 amu; Figure 3 shows the results obtained for 26 amu. Only one peak is seen for this species, and only after exposures above 5 L. This feature is initially centered around 330 K, but it broadens and shifts to lower temperatures

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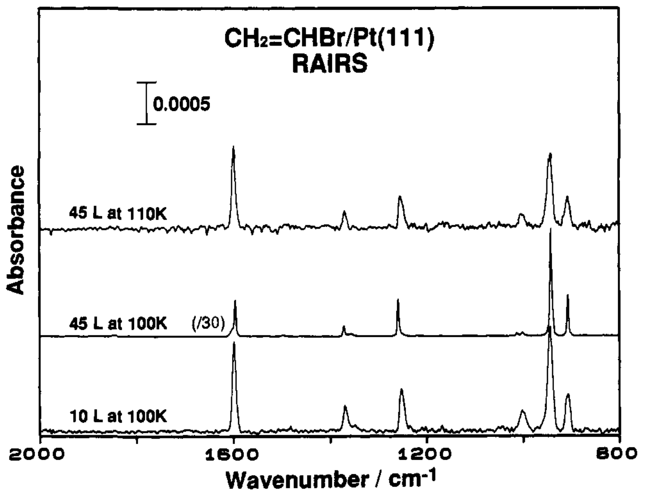

Figure 4. Reflection-absorption infrared (RAIRS) spectra for vinyl bromide adsorbed on Pt(111) at 90 K as a function of initial exposure.

Table 1. Vibrational Assignment: Vinyl Halides Adsorbed on Pt(111)

	$CH_2{=}CHBr$		$CH_2{=}CHI$		
	adsorbed[a]	gas[b]	multilayer[a]	adsorbed[a]	liquid[c]
ν(C–H), A′	3078	3075	3059	3059	3060
combination			1704	1713	
ν(C=C), A′	1595	1596	1584	1584	1593
$\gamma(CH_2)$, A′	1370	1373	1367	1367	1376
combination			1263	1260	1250
δ_{in}(CH), A′	1258	1256	1230	1231	1229
$\delta_{in}(CH_2)$, A′	1000, 1011	1006	985	987	990
δ_{out}(CH), A″	941	942	948	946	946
$\rho_{out}(CH_2)$, A″	906	902	913	910	909

[a] This work. [b] Reference 28. [c] Reference 29.

with increasing coverages until reaching a peak value of 290 K at saturation. The behavior observed here is similar to that reported for ethylene adsorbed on a clean surface, a fact that suggests that ethylene detection in the vinyl iodide case is desorption limited. Again, the features observed below 200 K are due to molecular desorption.

The TPD data reported above was complemented with reflection-absorption infrared spectroscopy (RAIRS) studies on the adsorption and thermal reactivity of both vinyl bromide and vinyl iodide. Vinyl bromide adsorbs molecularly on Pt(111) at liquid nitrogen temperatures but desorbs intact around 110 K; the most relevant infrared spectra for this system are shown in Figure 4 and summarized in Table 1. The main vibrational modes in vinyl bromide start to appear at very low coverages and grow in intensity with increasing temperatures, and the trace for a 10 L exposure, which corresponds to a coverage close to a monolayer, already displays all the features associated with vinyl bromide in liquid, solid, or gas phases (Figure 4, bottom trace). Furthermore, multilayer desorption after large exposures restores the spectrum seen for the original monolayer (top trace). There are, nevertheless, subtle differences with the multilayer spectra (middle trace): for one, the features in the monolayer spectra are broader than those in the multilayer, and moreover, the peaks due to the out-of-plane CH and CH_2 deformations grow first at low coverages, but the peak due to the C–C bond stretching mode then grows to become the dominant feature in the spectrum for the monolayer. Using the dipole metal surface selection rule that applies to RAIRS experiments[30] we interpret the latter observations as the consequence of an initial flat adsorption geometry that switches to another where the molecular axis is at a large angle (although not perpendicular) from the surface plane when monolayer saturation is reached.

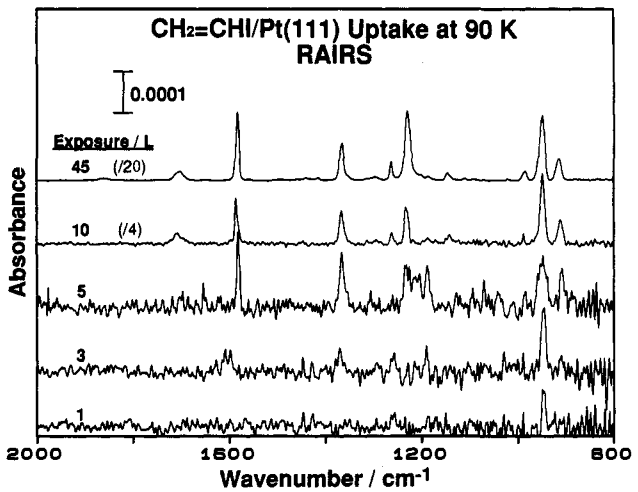

Figure 5. RAIRS spectra for vinyl iodide adsorbed on Pt(111) as a function of initial exposure.

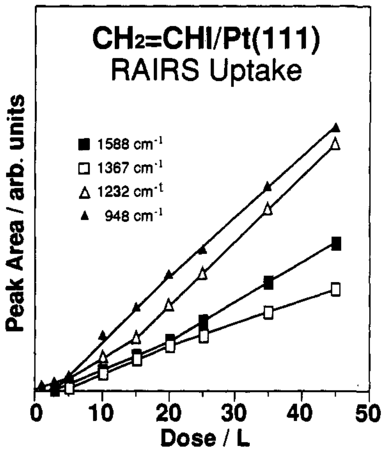

Figure 6. RAIRS signal intensities as a function of initial exposures for the main spectral features observed in the low temperature adsorption uptake of vinyl iodide on Pt(111). These data were obtained from the analysis of the spectra displayed in Figure 5.

Figure 5 shows infrared spectra for vinyl iodide adsorbed on Pt(111) at 90 K as a function of initial exposure. The spectrum obtained for the multilayer (top trace) displays the same peak positions and relative intensities as those obtained for liquid samples and as those reported in the literature; the results are also summarized in Table 1. At low coverages only the peak at 948 cm^{-1} (due to the C–H out of plane deformation) is visible, indicating that the molecule must be oriented with its axis parallel to the surface because the C–H deformation is the only vibrational mode with a dynamic dipole moment perpendicular to the molecular plane.[30] After a 5 L exposure other modes due to molecular vinyl iodide grow in the spectrum, namely, those at 913, 1230, 1367, and 1584 cm^{-1}, and, in addition, a couple of extra features are seen around 1190 and 1210 cm^{-1} which could be assigned to vinyl species directly adsorbed on the platinum surface. By 10 L, which still represents only about 70% of saturation, the spectra already resembles quite closely that of the multilayer, except for a few small differences in the relative intensities of the main features (Figure 6): both the C–C stretching and the in-plane C–H deformation display slightly lower relative intensities than those corresponding to liquid vinyl iodide, indicating that although the molecule may be somewhat inclined, it still prefers a small tilting angle at this coverage.

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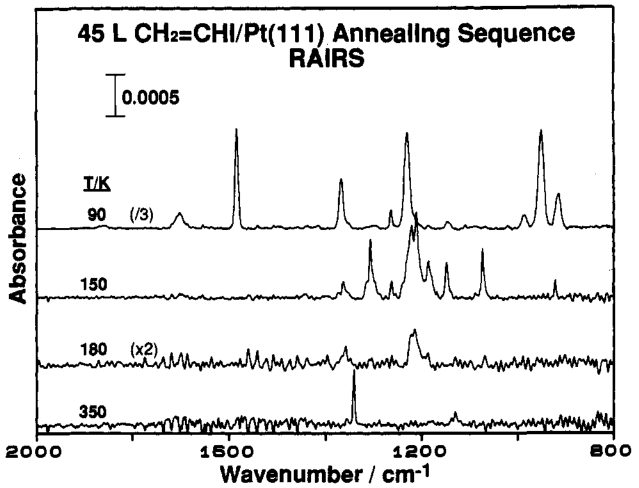

Figure 7. RAIRS spectra as a function of annealing temperature for 45 L vinyl iodide dosed on Pt(111) at 90 K.

Table 2. Vibrational Assignment Species A (130–170 K)

	this work	$Os_3(CO)_9(\mu\text{-}H)_2$ $(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)^a$	$Ru_2(CO)_3(\eta^5\text{-}Cp)_2$ $(\mu_2\text{-}C{=}CH_2)^a$
$\rho_{wag}(CH_2)$	921	963	973
$\rho_{rock}(CH_2)$	1071	1051	988
$\nu(CC)$	1306	1331	1586
$\gamma(CH_2)$, $\nu(CC)$	1440	1470	

^{a} Reference 31.

Figure 7 displays the most relevant infrared spectra related to the thermal chemistry of vinyl iodide chemisorbed on Pt(111). The spectrum at the top, which corresponds to a vinyl iodide multilayer condensed at 90 K and which matches the top trace in Figure 5, has already been discussed above. After heating to 150 K no vibrational peaks due to vinyl iodide are observed in the RAIRS data anymore (according to the TPD data molecular desorption is over by then), but a series of new peaks develop in the spectra. These new features can be grouped in two sets, one that includes the sharp signals at 921, 1071, and 1306 cm^{-1}, which grows around 130 K and disappears by 170 K, and another with the remaining bands at 1147, 1184, 1209, 1220, 1261, and 1360 cm^{-1}, which also appears around 130 K but persists until about 200 K.

The identification of the species that form in the 130–200 K temperature range can be made by comparing the RAIRS data to reported spectra for organometallic clusters. The first moiety (species A, the one that disappears around 170 K) can be identified as μ_3-η^2-vinylidene (Pt_n·C·CH_2) this way (Table 2);[31] not only it is clear that the species in question consists of a vinyl moiety, but the specific assignment to a μ_3-η^2 bonding arrangement is also easily justified by the fact that a μ_2 coordinated vinylidene group displays a significantly different infrared spectrum (Table 2). The unequivocal identification of species B (the one that persists until annealing above 200 K), however, is a bit more difficult, since not many hydrocarbon fragments display strong vibrational modes in the 1200–1250 cm^{-1} range; the best match we were able to obtain was with data from acetylene moieties both in metallic clusters and adsorbed on metal surfaces (Table 3). The similarity with the data reported for the Fe(110) system[32] is particularly good, since the most dipole active modes in both cases are those seen around 1220–1260 cm^{-1}. Moreover, according to the data reported in the literature the most probable coordination mode for this acetylene would be a μ_3-η^2 configuration with the molecular axis parallel to the surface;[35,36] as in the case of vinylidene, these vibrational data are quite sensitive to the geometrical arrangement.[37,38] The multiple bands observed in our spectra could be interpreted as the result of the presence of two unequivalent adsorption sites. Acetylene adsorbed directly on a clean Pt(111) surface yields a very different vibrational spectrum, with peaks centered around 770, 990, 1130, 1310, and 3010 cm^{-1},[19,39] but the difference between that data and ours is perhaps due to the presence of coadsorbed iodine atoms in the latter case. An alternate although somewhat less convincing assignment of species B to a vinyl moiety could be argued by comparison with the spectrum of $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)(\mu\text{-}\eta^2\text{-}CH\text{-}CH_2)]BF_4$.[31] Even though the main infrared frequencies for such complex are seen at 844, 1301, 1421, 1433, and 1468 cm^{-1}, the additional peaks observed at 1100–1150, 1220, 1285, and 1356 cm^{-1} could be matched with the ones in our data at 1147, 1184, 1220, 1261, and 1360 cm^{-1}, and the differences in relative intensities could be explained by orientational effects in the adsorbed system (a nearly flat adsorption geometry of the vinyl group). The comparison is certainly not very good, and in any case, the infrared spectra reported for $Os_3(CO)_{10}(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CH{=}CH_2)$,[31,40] a better model for the surface system, is quite different to the one obtained in our study.

Table 3. Vibrational Assignment: Species B (130–200 K)

	this work	$C_2H_2/Fe(110)^a$	$C_2H_2/Ni(111)^b$	$Os_3(CO)_{10}$ $(\mu_3\text{-}\eta^2\text{-}HCCH)^c$
$\delta_s(CH)$	1147,1184	1150	1080	1032
	1209			1203
$\nu(CC)$	1220,1261	1240	1220	1228
$\delta_a(CH)$	1360	1415	1370	1297

^{a} Reference 32. ^{b} Reference 33. ^{c} Reference 34.

Further heating of the sample results in additional transformations of the surface species: by 200 K no visible features are observed in the infrared spectra, around 300 K a new spectrum characteristic of ethylidyne moieties develops (with two peaks at 1128 and 1340 cm^{-1}),[3] and heating above 500 K eliminates any detectable IR signal again. The saturation coverage for vinyl iodide on Pt(111) can be estimated by using the infrared signal intensities obtained for ethylidyne, which in the case of the decomposition of adsorbed vinyl iodide amounts to about half of those observed when starting from ethylene. Assuming a coverage of a quarter of a monolayer for the latter case,[41] the coverage of the former comes out to be about $\Theta = 0.12$–0.13. Since the molecular TPD data indicate that less than half of the adsorbed vinyl iodide desorbs intact from the first layer (molecular desorption starts above 7.5 L and saturation is reached about 15 L; it is reasonable to assume that the sticking coefficient is constant with coverage,[24] and ethylene desorption is expected to amount to about 30% of ethylidyne formation,[42,43]) the initial saturation coverage at liquid nitrogen temperatures is estimated to be of the order of 30–35% of a monolayer. This is consistent with previous reports.[24]

4. Discussion

The results reported here allow for the development of a reasonably complete picture for the chemistry of vinyl iodide on Pt(111) surfaces. To begin with, adsorption at liquid nitrogen temperatures is probably mostly molecular, although such a

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statement cannot be fully supported by our experiments. Based on HREELS and TPSIMS results Liu et al. report that dissociation of up to about 30% of the vinyl iodide at saturation occurs at temperatures as low as 105 K, but their iodine XPS data indicate that complete C–I bond scission takes place only above 165 K.[24] What is clear from our data is that there is a change in adsorption geometry as the coverage increases: only the peak around 950 cm^{-1} is observed in the IR spectra for doses below 5 L, an observation that we interpret as the result of an initial adsorption where the molecule lies flat on the surface, but above 5 L other vibrational modes become apparent, presumably because of a switch in the orientation of the adsorbates into a tilted configuration; geometry changes like this have in fact been reported before for both alkyl halides and alkyl moieties on similar surfaces.[26,44]

This change in adsorption geometry with coverage most likely induces some changes in the subsequent thermal chemistry of the adsorbed vinyl iodide molecules. At low coverages (below 5 L) the lying-flat molecules most probably decompose completely at low temperatures, since only hydrogen desorbs from the surface, but at saturation the chemistry is certainly more complex, even though the determination of what takes place during the initial steps in that case is somewhat obscured by the concomitant occurrence of some molecular desorption. The first identifiable change in our infrared data is the appearance of signals for two new species, which we propose are vinylidene and acetylene. However, the conversion of vinyl iodide to those moieties may not be an elementary step but may go through a vinyl metastable intermediate instead. For one, the C–I bond is much weaker than any of the C–H bonds (60 versus 100 kcal/mol) and is therefore expected to break first. Moreover, adsorbed vinyl iodide reacts with coadsorbed deuterium to yield mainly monodeuteriated ethylene,[24] suggesting that a reductive elimination step may take place between deuterium atoms and vinyl species. In any case, if vinyl is formed at all, it must decompose quite rapidly, because no convincing spectroscopic evidence was obtained to support its presence on the surface at any stage of the thermal activation.

Regardless of if vinyl iodide decomposes into vinyl moieties or not at lower temperatures, heating to 140 K yields a mixture of vinylidene and acetylene species on the surface. The simultaneous formation of those two species may seem somewhat surprising, but similar reactions have in fact been seen in organometallic systems. For one, clusters with coordinated vinyl,[45–55] vinylidene,[48–59] and acetylene[46–49,57] ligands have all been prepared starting from either ethylene or acetylene, and structures (characterized by X-ray and neutron diffraction) with μ_3-η^2 configurations similar to those proposed here on the platinum surface have in fact been shown to be the most common in trimetallic clusters.[46,60–62] Furthermore, some conversions have also been reported for vinyl to vinylidene[48–51,53,54] and to acetylene,[48] for acetylene to vinyl,[46,63] for vinylidene to acetylene,[49] and for acetylene to vinylidene.[64] It would seem as if the coordination of either vinylidene or acetylene on metal clusters requires energies comparable to those required for the adsorption of the same species on solid surfaces.[48,57]

The vinylidene that forms around 140 K then disappears about 170 K, while the coadsorbed acetylene subsists up to by 200 K. No vibrational features are then seen in the infrared spectra between 200 and 300 K, even though the platinum surface must still be covered with a hydrocarbon fragment in this temperature range, since annealing to 300 K does bring back some infrared absorption intensities (now associated with the formation of ethylidyne). The lack of IR features between 200 and 300 K can be explained either by a lack of instrumental sensitivity or by the existence of species that only have vibrational modes with dynamic dipoles parallel to the surface plane. The latter possibility leads us to propose the formation of ethylene on the surface. Since some ethylene does desorb between 240 and 320 K, the same temperature range as that seen from chemisorbed C_2H_4 (Figure 3), it could be possible that ethylene does form on the surface around 200 K but desorbs at higher temperatures; the detection of ethylene in the TPD experiments may be limited by the rate of its desorption. Previous experiments have shown that adsorbed ethylene is indeed difficult to identify by RAIRS,[27,65] since the spectra for saturation coverages of ethylene ($\Theta = 0.25$) display only weak peaks around 991 and 1048 cm^{-1} (their intensities being below 2×10^{-4} AU). The total amount of ethylene produced in the vinyl system is less than half of that surface concentration, so we suspect that the signal in this case is lost in the noise. It should also be mentioned that even though ethylene molecules contain more hydrogen atoms per carbon than the original vinyl iodide, it is not hard to conceive hydrogen incorporation either from background adsorption or from decomposition of a minor fraction of the surface species in order to fulfill the new H/C ratio.

Finally, the identification of ethylidyne around 300 K is clear. It has already been well-established that the thermal activation of ethylene yields ethylidyne on quite a number of surfaces[1] and that the same species also forms from ethyl moieties, in that case via an intermediate β-hydride elimination step that yields surface ethylene.[23,27,66] The formation of ethylidyne on the surface by heating adsorbed vinyl iodide would also be expected if ethylene is indeed produced in that case, but its direct formation from vinylidene[51,67] or from acetylene[47] is also quite possible, since that reaction has been reported to take place in organometallic systems. Finally, ethylidyne decomposes above 500 K. The overall proposed reaction network for vinyl iodide decomposition on Pt(111) is shown in Scheme 1.

The results from the studies of the surface chemistry of vinyl species on Pt(111) presented here shed some light into the mechanism for the conversion of ethylene to ethylidyne. As mentioned in the introduction, several pathways have been reported in the literature for this reaction, but none has been

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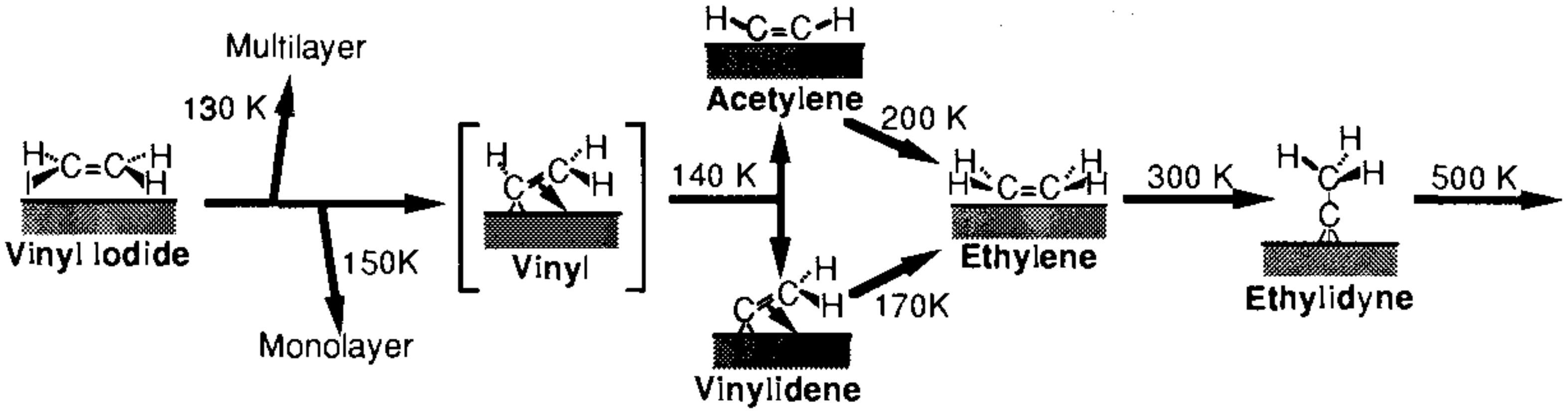
Scheme 1. Vinyl Iodide Thermal Chemistry on Pt(111)



proven conclusively. Any mechanism that tries to explain this reaction must account for at least two changes in the surface moieties, namely, the removal of a hydrogen atom from the ethylene molecule (the breaking of a C–H bond), and the transfer of a second hydrogen from one carbon to the other. Given that such steps are also accompanied by a collective geometrical rearrangement of the whole molecule and by a change in hybridization, it is difficult to visualize any type of mechanism where all these processes take place in a concerted fashion. In view of this, two relatively simple reaction sequences can be proposed which lead to the ethylene–ethylidyne transformation, one in which the hydrogen removal takes place first and the hydrogen transfer later, in which case a vinyl-like intermediate would form, and a second one in which these steps are reverse, namely, where the hydrogen transfer step occurs first, and where formation of ethylidene moieties takes place instead ($CHCH_3$). Since no intermediates have been detected during the ethylene–ethylidyne conversion (even though recent careful kinetic experiments do suggest that there could be a small accumulation of such species under certain conditions,[68]) the first step of the overall reaction must be the rate limiting one. Working with these hypotheses we recently performed some experiments with triply labeled ethylene ($CHD{=}CD_2$) that lead us to conclude that the hydrogen atom involved in that first limiting step is the same that later desorbs in TPD experiments around 300 K;[18] such a conclusion is inconsistent with the participation of ethylidene moieties in a simple two step mechanism and therefore favors vinyl formation. The fact that vinyl intermediates may be stable on metal surfaces is also supported by results from studies on the decomposition of ethylene on Ni(100), where such species was isolated above 170 K.[69,70] Unfortunately, no ethylidyne formation takes place in that system.

The ideas discussed above need to be reevaluated in view of the results presented in this paper. Our data indicate that vinyl moieties can indeed be converted into ethylidyne, but only by going through a series of transformations that not only involve the formation of both vinylidene and acetylene but also that most likely include ethylene production. These results suggest that ethylene is more stable than vinyl on Pt(111) surfaces and that the conversion of the latter into the former occurs around 200 K and is probably irreversible. This is not to say that vinyl cannot be converted into ethylidyne directly in other systems: such reaction has in fact been reported in several organometallic systems,[47,71] but only that it does not seem to be consistent with the experimental observations gathered for the Pt(111) case. It could also be argued that the results reported here for vinyl iodide are not relevant to the chemistry of ethylene on clean Pt(111) surfaces because the codeposited iodine atoms may modify the surface chemistry of the adsorbed hydrocarbon species significantly. Several tests have been done to date to try to assess the magnitude of this problem. For one, vibrational (and other) spectra obtained for species such as ethylidyne formed by decomposition of alkyl iodides (ethyl iodide in this case) have been shown to be identical to those acquired after preparing the same species by other means (by activating ethylene).[23] Furthermore, the olefins produced by β-hydride elimination in alkyl groups (from alkyl iodides) on Pt, Ni, and Cu surfaces have shown similar reactivity to that seen when the corresponding olefin is directly adsorbed on the clean surfaces.[72-74] Finally, the chemistry of methyl iodide on Pt(111) and Cu(111) surfaces has been favorably compared to that of species prepared by adsorption of gas phase methyl free radicals.[75,76] It is now widely believed that iodine atoms act as site blockers in these systems but do not alter significantly the electronic properties of the surface.

At the present time we are at a bit of a lost as to what simple mechanism is capable of explaining the ethylene–ethylidyne conversion. One possible answer to this quandary may come from a more careful analysis of the arguments used to rule out ethylidene as an intermediate. It is true that a mechanism consisting of only two steps with ethylidene as an intermediate would not account for the results obtained in the isotopic labeling TPD experiments, but one where a fast ethylene–ethylidene equilibrium is set at low temperatures (shifted to the left so the ethylidene concentration remains below any detection levels) and where the overall rate is limited by the conversion of ethylidene to ethylidyne could account for the kinetic results reported for C_2D_3H, because the isotope effects on the steady-state concentrations of ethylidene would be smaller than that for the second ethylidene–ethylidyne conversion. To illustrate this point, lets assume that in the mechanism

$$\begin{array}{ll} CX_2{=}CX_2\ (ad) \rightarrow CX{-}CX_3\ (ad) & k_1,\ \text{fast} \\ CX{-}CX_3\ (ad) \rightarrow CX_2{=}CX_2\ (ad) & k_{-1},\ \text{fast} \\ CX{-}CX_3\ (ad) \rightarrow C{-}CX_3\ (ad) + X\ (ad) & k_2,\ \text{slow} \end{array}$$

(where X stands for either H or D) the isotope effects for k_1 and k_{-1} are comparable and that $k_2(H) = 3k_2(D)$. From this we can calculate the relative equilibrium constants for the formation of both $CH{-}CD_3$ and $CD{-}CHD_2$ from $CHD{=}CD_2$, which are controlled by a statistical factor that depends on the stoichiometry of the initial compounds. That is,

$$K(CH{-}CD_3) = \frac{1}{3}K(CD{-}CHD_2)$$

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and therefore

$$[\mathrm{CH{-}CD_3}]_{\mathrm{eq}} = \frac{1}{3}[\mathrm{CD{-}CHD_2}]_{\mathrm{eq}}$$

The rates for ethylidyne formation can then be calculated according to the formulas

$$R(\mathrm{C{-}CD_3}) = k_2(\mathrm{H})[\mathrm{CH{-}CD_3}]_{\mathrm{eq}}$$

and

$$R(\mathrm{C{-}CHD_2}) = k_2(\mathrm{D})[\mathrm{CD{-}CHD_2}]_{\mathrm{eq}} = \{{}^1/_3 k_2(\mathrm{H})\}\{3[\mathrm{CH{-}CD_3}]_{\mathrm{eq}}\} = R(\mathrm{C{-}CD_3})$$

So this back-of-the envelope calculation shows that the mechanism given above can indeed explain the enhancement in both the formation of fully deuterated ethylidyne and the desorption of normal hydrogen from activation of $\mathrm{CHD{=}CD_2}$. We are presently setting up to study the thermal chemistry of ethylidene moieties to test these ideas.

Finally, mechanisms that start with hydrogen incorporation and ethyl formation cannot be completely ruled out.[7] We, however, do not favor that type of scheme for two reasons: one, because ethylidyne formation takes place at temperatures comparable to those where hydrogen recombination and molecular H_2 desorption take place,[77] so any hydrogen incorporation reaction would have to compete with such desorption; and two, because the conversion of ethyl groups into ethylene (a β-hydride elimination step) takes place readily at quite low temperatures,[23,27,66] so the reverse reaction is not expected to contribute significantly to the overall mechanism. More experiments are needed in order to settle these mechanistic questions.

5. Conclusions

We have shown here that the thermal chemistry of vinyl iodide adsorbed on Pt(111) surfaces is quite complex. The first step presumably involves the scission of the C–I bond to yield vinyl surface moieties, but such reaction, if it occurs, is immediately followed by a couple of competitive dehydrogenation steps to produce vinylidene and acetylene. Vinylidene decomposes further around 170 K, while acetylene is stable until reaching temperatures close to 200 K. At that point both intermediates disappear to form a new species, possibly ethylene. Finally, annealing the surface to above 300 K yields ethylidyne groups, which are stable to up to 500 K. These results bring to question some of the earlier interpretations of the mechanism for the transformation of ethylene to ethylidyne on platinum surfaces.

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