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The conversion of di- σ bonded ethylene to ethylidyne on Pt(111) monitored with sum frequency generation: evidence for an ethylidene (or ethyl) intermediate

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Abstract

The conversion of di- σ bonded ethylene ($-\text{CH}_2-\text{CH}_2-$) to ethylidyne ($\equiv\text{CCH}_3$) on the Pt(111) crystal surface was monitored with infrared–visible sum frequency generation (SFG) in the $\nu(\text{CH})$ frequency range. The conversion began around 255 K and involved a third stable species that is neither di- σ bonded ethylene nor ethylidyne. This species manifested itself as a peak at 2957 cm^{-1} in the vibrational spectrum. Furthermore, we found the same species present during the conversion of vinyl iodide to ethylidyne on Pt(111). The 2957 cm^{-1} feature has been assigned to the CH_3 asymmetric stretch of ethylidene and/or ethyl.

Keywords: Ethylidyne; Sum frequency generation

1. Introduction

When ethylene is chemisorbed on the (111) crystal face of platinum at temperatures in the range of 120–240 K, di- σ bonded ethylene ($-\text{CH}_2\text{CH}_2-$) forms [1–3]. Annealing this species above 280 K causes ethylidyne ($\equiv\text{CCH}_3$) to form [4]. Ethylidyne is adsorbed in an fcc threefold hollow site with its

C–C axis perpendicular to the surface. Its structure and the relocation of platinum atoms around the site have been reliably determined by tensor LEED surface crystallography [5]. The transformation of di- σ bonded ethylene to ethylidyne is shown schematically in Fig. 1. The purpose of this paper is to investigate the mechanism of this transformation by spectroscopic identification of possible intermediate species. To this end we carried out vibrational spectroscopy studies, using the technique of optical sum frequency generation (SFG) on the (111) crystal face of platinum in the temperature range of 202–352 K.

Several different mechanisms involving the formation of a variety of intermediates have been pro-

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Fig. 1. Decomposition of ethylidyne on Pt(111).

posed in the literature. These intermediates include ethyl groups ($\text{CH}_3\text{--CH}_2\text{--}$) [6], vinyl groups ($\text{CH}_2=\text{CH--}$) [7,8], ethylidene (--CH--CH_3) [9,10], and vinylidene ($=\text{C=CH}_2$) [11,12]. Because direct spectroscopic evidence for any of these intermediates has been elusive, it has been widely assumed that the rate limiting step for this reaction is either the breaking of the first CH bond in the di- σ bonded species to form vinyl [7,8] or the isomerization of the adsorbed di- σ bonded species to ethylidene [9,10].

Although direct spectroscopic evidence has been lacking, some experimental and theoretical studies have pointed to the likelihood of a mechanism involving an ethylidene intermediate. Windham and Koel have shown spectroscopic evidence for ethylidene formation on Pt(111) when ethylene is coadsorbed with 0.12 monolayers of potassium at 100 K and then annealed to 300 K [10]. Evidence for an ethylidene species in the potassium promoted system has been further supported by Zhou et al. using secondary ion mass spectroscopy (SIMS) [13]. Some theoretical evidence has also pointed to ethylidene as a possible reaction intermediate. Carter and Koel have made equilibrium thermodynamic estimates of the energetics of the transformation of di- σ bonded ethylene to ethylidyne [9]. These estimates support a mechanism involving ethylidene. However, it should be noted that other theoretical studies did not support this conclusion [12,14]. In fact some experimental evidence points to vinyl intermediates [7,8].

In the present work we utilize infrared–visible sum frequency generation to study the $\nu(\text{CH})$ portion of the vibrational spectrum ($2700\text{--}3100\text{ cm}^{-1}$). SFG is a powerful technique for surface vibrational spectroscopy because it is both surface specific and capable of providing resolution on the order of 10 cm^{-1} or less. The $\nu(\text{CH})$ portion of the vibrational spectrum is extremely valuable because of the frequent difficulty in interpreting the complex structure often found in the $900\text{--}1500\text{ cm}^{-1}$ region of the spectrum.

SFG has been described in great detail in the literature [15–17]. Briefly, it is a second-order nonlinear optical process in which an infrared beam is combined with a visible beam to generate a sum-frequency output. The process is only allowed (in the dipole approximation) in a medium without inversion symmetry. The fcc lattice in the bulk of platinum is centrosymmetric and, therefore, in the case of an organic monolayer adsorbed on Pt(111) the SFG signal may be dominated by the contribution from the interface between the metal and vacuum. As the IR beam is tuned through vibrational resonances of surface species the effective surface nonlinear susceptibility $\chi_S^{(2)}$ is resonantly enhanced. The SFG signal is proportional to the absolute square of $\chi_S^{(2)}$ and, hence, a vibrational spectrum of the surface species is detected. Formally we can write:

$$\chi_S^{(2)} = \chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)},$$

$$\chi_{\text{R}}^{(2)} = \sum_q \frac{A_q}{\omega_{\text{ir}} - \omega_q - i\Gamma_q}, \quad (1)$$

where $\chi_{\text{NR}}^{(2)}$, $\chi_{\text{R}}^{(2)}$, A_q , ω_q , ω_{ir} , and Γ_q refer to the nonresonant nonlinear susceptibility, resonant nonlinear susceptibility, strength of the q th vibrational mode, q th vibrational mode, infrared laser frequency, and the damping constant of the q th vibrational mode respectively.

Our results indicate the presence of a third species present on the Pt(111) surface during the conversion of di- σ bonded ethylene to ethylidyne. This species gave rise to a vibrational feature which was observed only during the reaction and has been assigned to the CH_3 asymmetric stretch of ethylidene and/or ethyl.

2. Experimental

All experiments were carried out in an ultra high vacuum chamber pumped with a turbo pump and an ion pump. The chamber had a base pressure of less than 1×10^{-10} Torr and was equipped with a Varian retarding field analyzer (RFA) for Auger and LEED, a high resolution electron energy loss spectrometer (HREELS), a VG SX300 mass spectrometer, and CaF_2 windows to allow the passage of infrared and visible laser beams. The Pt(111) crystal used in this experiment was spot welded onto the manipulator

Fig. 2. Apparatus for UHV-SFG.

with platinum wires and was capable of being resistively heated to above 1200 K and cooled with liquid N_2 to 115 K. Temperature was measured with a chromel–alumel thermocouple which was positioned on the edge of the crystal. The sample itself was cut, polished, and then cleaned in UHV following the standard procedures.

A 20 picosecond passive, active mode-locked Nd:YAG laser with a maximum output energy of 50 mJ/pulse at 1064 nm was used to perform the SFG. A portion of the beam was frequency doubled to 532 nm and used as the visible portion of this spectroscopy. The rest of the light was sent to a $LiNbO_3$ optical parametric generator/amplifier arm where it could be frequency tuned from 2650–3900 cm^{-1} . The two beams were then focused concentrically

onto the Pt(111) sample. Both the green and IR light used in this experiment were p-polarized such that their electric fields had components perpendicular to the surface of the platinum crystal. The sum frequency photons generated from the crystal surface were detected via a photomultiplier tube and the signal was stored on a microcomputer. Fig. 2 is a schematic diagram of the instrumentation.

In this experiment 4 L of ethylene (Matheson, C.P. grade) were dosed onto clean Pt(111) at 202 K. The crystal was cooled to 120 K at which point an SFG spectrum was taken. The crystal was then annealed to successively higher temperatures for periods of 60 s after which the crystal was allowed to cool to 120 K. At the conclusion of each such process an SFG scan was taken at 120 K. Additional spectra of di- σ bonded ethylene on Pt(111), ethyldyne on Pt(111), and vinyl iodide (99% pure, Pfaltz and Bauer) on Pt(111) were taken for comparison. All spectra presented in this study represent raw data.

3. Results

Fig. 3a represents a scan of ethylene adsorbed onto clean Pt(111) at 300 K and then flashed to 400

Fig. 3. (a) 4 L of ethylene dosed on Pt(111) at 300 K and flashed to 400 K. (b) 4 L of ethylene dosed on Pt(111) at 202 K, spectrum taken at 120 K.

K, a procedure which completely decomposes chemisorbed ethylene to ethylidyne. The spectrum shows only one major feature at 2885 cm^{-1} (unfitted value) representing the CH_3 symmetric stretch of ethylidyne. A second much smaller feature just under 2800 cm^{-1} has been assigned to a Fermi resonance with an asymmetric bending mode [18]. The nonresonant background signal immediately beyond the peak frequency falls below its base line and then returns. This is the interference pattern formed from the interplay between the nonresonant background signal (in this case due primarily to the platinum surface) and the resonant signal from the ethylidyne species. Because of this interaction, the peak of the resonant feature comes at a slightly lower frequency than would otherwise be expected. Signal in a sum frequency experiment is proportional to the square of Eq. (1); therefore, fitting the data by $|\chi_s^{(2)}|^2$ yields the actual resonant frequency of the main peak in Fig. 3a at 2886 cm^{-1} . All further peaks in this paper have been identified by their fitted value for the resonant frequency.

Fig. 3b is a scan of di- σ bonded ethylene that has been adsorbed on Pt(111) at 202 K and then cooled to 120 K before taking the spectrum. The singular feature in this spectrum is at 2904 cm^{-1} and has been assigned to a CH_2 symmetric stretch [1–3]. From reflection–adsorption infrared spectroscopy (RAIRS) studies, Hoffman et al. have concluded that the CH_2 asymmetric stretch is also incorporated under this peak [19].

Fig. 4 shows a series of eight spectra of di- σ bonded ethylene annealed to successively higher temperature. During the annealing process di- σ bonded ethylene is converted to ethylidyne. Upon annealing di- σ bonded ethylene to 243 K for 60 s the CH_2 symmetric stretch peak shifts to 2906 cm^{-1} and sharpens up, but the spectrum remains otherwise unchanged from the spectrum in Fig. 3b. The first sign of significant change begins as the sample is annealed to 257 K. There is a definite decrease in intensity of the CH_2 symmetric stretch peak and a new feature begins to grow in around 2953 cm^{-1} . Further, a shoulder which is assigned to the CH_3 symmetric stretch of ethylidyne develops on the low frequency side of the CH_2 peak.

The ethylidyne shoulder feature increases slightly as the sample is annealed to 265 K. The drop off in

intensity of the CH_2 peak continues as its frequency shifts to 2916 cm^{-1} . The high frequency feature shifts to 2957 cm^{-1} and continues to grow. Annealing to 273 K for 60 s makes the CH_3 symmetric stretch at 2889 cm^{-1} of the growing ethylidyne resonance clearly visible. The CH_2 symmetric stretch peak which has now shifted to 2918 cm^{-1} has decayed substantially while the high frequency feature continues to grow. At 281 K the CH_2 symmetric stretch has almost completely disappeared. The CH_3 symmetric stretch peak of ethylidyne continues to increase in intensity and the 2957 cm^{-1} stretch peak starts to decrease.

Annealing to 288 K shows continued growth of the ethylidyne peak while the high frequency feature has nearly disappeared. Further annealing to 296 K and then 352 K leaves only the CH_3 symmetric stretch of ethylidyne.

Fig. 4. 4 L of ethylene dosed on Pt(111) at 202 K is annealed stepwise from 243 to 352 K.

4. Discussion

The CH stretch portion of the vibrational spectrum shows a clear progression from di- σ bonded ethylene to ethylidyne with the appearance of a high frequency feature at 2957 cm^{-1} that is only present during the transition (Fig. 4). The primary objective of this discussion is to identify this feature. There are several candidates for this species, including ethyl, ethylidene, vinyl, and vinylidene. A possible asymmetric stretch mode and a Fermi resonance of both di- σ bonded ethylene and ethylidyne must also be considered.

The possibility that the high frequency feature is a Fermi resonance can be discounted because its signal would have to grow and attenuate in concert with either the CH_2 or CH_3 symmetric stretch resonance. This is not the case for either the CH_2 or CH_3 mode. The 2957 cm^{-1} peak remains until after the CH_2 symmetric stretch intensity is completely gone and actually attenuates as the CH_3 symmetric stretch grows. Further, neither the di- σ bonded ethylene nor the ethylidyne species when present alone on the surface have Fermi resonances in the 2957 cm^{-1} range.

The high frequency feature in Fig. 4 is also unlikely to be from an asymmetric stretch mode. Although asymmetric stretches of CH_3 species on Pt(111) are found in this region of the spectrum, they are mostly forbidden in the ethylidyne geometry because of the surface dipole selection rule, which requires the dynamic dipole moment of the species to have some component normal to the surface. In this case (with the C–C bond axis normal to the surface) the asymmetric stretch would be in plane with the surface and would not appear in this spectroscopy. In fact the asymmetric stretch feature is not observed in the pure ethylidyne spectrum (Fig. 3a).

It also cannot be argued that the high frequency feature is from the CH_2 asymmetric stretch of di- σ bonded ethylene. This is because the high frequency peak is clearly still present *after* the CH_2 symmetric stretch signal has completely vanished. For this feature to be the CH_2 asymmetric stretch, there would have to be a conformation of di- σ bonded ethylene that would only allow the asymmetric stretch to be observed, but not the symmetric one. It is extremely difficult to envision such a conformation of di- σ

bonded ethylene on Pt(111). This leads to the conclusion that the high frequency stretch seen during the conversion is due to a species that is neither di- σ bonded ethylene nor ethylidyne, but rather a third species that is only present on the surface during the conversion of the former into the latter.

Both a vinyl group ($-\text{CH}=\text{CH}_2$) and vinylidene group ($=\text{C}=\text{CH}_2$) can be ruled out as a candidate for the 2957 cm^{-1} feature. Infrared and Raman spectra of vinyl and vinylidene moieties in osmium clusters show that the CH_2 symmetric and asymmetric stretches of these moieties occur too high (2998 , 3052 cm^{-1} for vinyl and 2990 , 3052 cm^{-1} for vinylidene) to account for this feature and the very weak CH stretch of vinyl is too low (2920 cm^{-1}) [20]. Further, a recent RAIRS study by Zaera et al. has shown that vinyl moieties decompose to acetylene and vinylidene by 140 K instead of directly converting to ethylidyne [21]. In the RAIRS study heating above 200 K caused all spectroscopic features to disappear. This led Zaera to conclude that π -bonded ethylene must be formed around this temperature. The π -bonded ethylene would have its dynamic dipole parallel to the surface and would therefore not be seen by infrared spectroscopy. Zaera accounted for the change in C/H stoichiometry from C_2H_3 to C_2H_4 by proposing either adsorption of H_2 from the background or the evolution of surface hydrogen from the formation of a minor decomposition product. Upon heating this system above 300 K ethylidyne features were observed.

We have also investigated the thermal evolution of the vinyl iodide on Pt(111) system and the spectra are shown in Fig. 5. The bottom spectrum shows 10 L of vinyl iodide dosed on Pt(111) at 132 K. At this temperature some of the C–I bonds are broken and vinyl moieties are directly adsorbed on the platinum surface [8]. There are three peaks (2995 , 3033 , and 3068 cm^{-1}) observed for vinyl iodide adsorbed on Pt(111) at 132 K. The 2995 cm^{-1} resonance can be assigned to the CH_2 symmetric stretch of a mixed sp^2/sp^3 hybridized species of either vinyl or vinylidene [20]. The 3068 cm^{-1} peak may be due to the CH_2 asymmetric stretch of intact vinyl iodide [8]. The 3033 cm^{-1} feature, however, is harder to identify because it does not correspond well with any frequency from the inorganic cluster models of vinylidene, vinyl, or acetylene [20,22]. Because there

Fig. 5. 10 L of vinyl iodide dosed on clean Pt(111) at 130 K and then annealed to 285, 295, and 406 K.

is significant dehydrogenation just above 132 K [21], an additional surface species or a Fermi resonance may already be present at this temperature. At any rate all of the peaks in this spectrum come at too high of a frequency to account for the 2957 cm^{-1} feature seen in the di- σ bonded ethylene to ethylidyne transition.

Upon annealing the vinyl iodide/Pt(111) system to 285 and 295 K (middle spectra in Fig. 5) there is only one peak present which is nearly at the same position as the high frequency feature seen during the transition of di- σ bonded ethylene to ethylidyne in Fig. 4. Upon further heating to 406 K the CH_3 symmetric stretch resonance of ethylidyne is seen at 2878 cm^{-1} (top spectra in Fig. 5). This seems to suggest that while vinyl is not the species responsible for the high frequency feature observed in the di- σ bonded ethylene to ethylidyne conversion, vinyl decomposes through the *same* intermediate(s) in its transformation to ethylidyne as is found by directly dosing and then annealing ethylene. This is quite reasonable in light of the finding by Zaera that vinyl converts to π -bonded ethylene before converting to ethylidyne [21].

We assign the 2957 cm^{-1} feature to the CH_3 asymmetric stretch mode of ethylidyne and/or ethyl. There is a preponderance of evidence which supports this assignment. In a RAIRS study of deuterated and nondeuterated ethyl iodide on Pt(111) Hoffman et al. have shown that ethyl groups give rise to three features in the CH stretch region at 2857, 2914, and 2952 cm^{-1} . The highest frequency feature has been assigned to the CH_3 asymmetric stretch of the terminal methyl group [19]. We have repeated this work using our SFG system and obtained the same results. Hoffman et al. have shown that ethyl groups may adopt either an upright or flat geometry on the (111) surface of platinum. It is in the latter case that the CH_3 asymmetric stretch is most prominent in their vibrational spectra (dipole selection rule). The orientation was shown to be coverage dependent with flat lying species predominant at low surface coverages.

In the case of ethylidyne moieties, osmium cluster work by Anson et al. has shown that the CH_3 asymmetric stretch comes at 2950 cm^{-1} and is the strongest feature in the CH stretch region for this species [23]. Further, in the case of K promoted Pt(111), where ethylidyne has been identified as the stable intermediate in ethylene decomposition to ethylidyne, a peak in the CH stretch portion of the HREELS spectrum was seen at 2955 cm^{-1} [10]. The CH stretch frequencies and assignments of ethyl iodide on Pt(111) (from Ref. [19]) and ethylidyne moieties in $[(\text{CH}_3\text{CH})\text{Os}_2(\text{CO})_8]$ (from Ref. [23]) are given in Table 1.

It is significant that no intensity is seen in the 2850–2857 cm^{-1} range (corresponding to a CH_3 symmetric stretch) during the presence of the 2957 cm^{-1} feature. This is a demonstration of the orientational sensitivity of SFG on metal surfaces. The signal intensity of a vibrational mode in our SFG experiments scales as $\cos^6\theta$ [24], where θ is the angle between the surface normal and the direction

Table 1
Frequencies of ethyl and ethylidyne moieties (in cm^{-1})

$[(\text{CH}_3\text{CH})\text{Os}_2(\text{CO})_8]$	Assign- ment	CH_3CH_2 / Pt(111)	Assign- ment
2950	$\nu_{\text{as}}(\text{CH}_3)$	2952	$\nu_{\text{as}}(\text{CH}_3)$
2916	$\nu(\text{CH})$	2914	$\nu_{\text{t}}(\text{CH}_3)$
2905/2850	$\nu_{\text{s}}(\text{CH}_3)$	2857	$2\delta_{\text{a}}(\text{CH}_3)$

of the dynamic dipole moment of the surface species. In the case of upright ethylidene moieties the CH_3 symmetric stretch mode would make a 55° angle with respect to the surface normal, whereas the CH_3 asymmetric stretch mode would make a 35° angle with respect to the normal. This difference in angle would lead to nearly an order of magnitude greater signal intensity for the CH_3 asymmetric mode in an SFG experiment. For ethyl groups, low coverages (flat lying) showed little or no intensity in the 2857 cm^{-1} region even in RAIRS experiments where signal intensity scales only as $\cos^2\theta$ [19]. Therefore, it would be expected that flat lying ethyl groups would not give rise to a peak in the 2857 cm^{-1} region of an SFG spectrum where the orientational sensitivity is even more extreme.

Another significant observation from Fig. 4 is the blue shift of the 2906 cm^{-1} feature. One possible explanation is that the changing surface coverage of di- σ bonded ethylene causes this phenomenon. We have carried out experiments on the coverage dependence of the CH_2 symmetric stretch frequency which show that there is indeed a shift from 2924 cm^{-1} at low coverage up to 2904 cm^{-1} at saturation. Another possibility is that the shift is due to intensity from another vibrational mode of the intermediate species. This would be easiest to explain in terms of an ethylidene intermediate. For an ethylidene moiety that has its methyl group tilted close to the surface and its hydrogen pointing nearly straight up, one might expect to see some intensity from the weak CH stretch mode. This would also explain the lack of intensity near 2850 cm^{-1} , because the CH_3 symmetric stretch would be nearly parallel to the Pt surface. It would, however, be more difficult to explain the blue shift of the 2906 cm^{-1} peak in terms of an ethyl group. This is because an additional feature at 2857 cm^{-1} is not seen. The 2857 cm^{-1} intensity would be from a Fermi resonance of the 2914 cm^{-1} feature and should scale with it.

Because small amounts of ethane have been detected to desorb from the surface during ethylidyne formation [25,26], we postulate that some ethyl species may exist during the conversion of di- σ bonded ethylene to ethylidyne. However, studies of ethyl moieties have shown that ethyl groups decompose to form di- σ bonded ethylene and ethane at temperatures above 250 K on the Pt(111) surface

Fig. 6. Three possible dehydrogenation mechanisms for di- σ bonded ethylene to ethylidyne through an ethylidene intermediate.

[27,28]. Our spectra of the conversion show that the 2957 cm^{-1} feature is present on the surface without any di- σ bonded ethylene at 281 and 288 K (Fig. 4). This requires ethyl groups to survive for minutes under severe dehydrogenation conditions after all the di- σ bonded ethylene is gone. Further, our vinyl iodide spectra show that the same CH_3 asymmetric stretch signal occurs even under the condition of 25% less initial surface hydrogen. For these reasons we favor an ethylidene interpretation of the 2957 cm^{-1} feature.

An ethylidene interpretation of the 2957 cm^{-1} stretch leads to two important conclusions. Ethylidene would be a likely intermediate in the conversion of di- σ bonded ethylene to ethylidyne and the breaking of the CH bond on the α -carbon of ethylidene would be the rate limiting step in this reaction.

The mechanisms in Fig. 6 illustrate three possible pathways for ethylene decomposition to ethylidyne that involve an ethylidene intermediate. In the first mechanism di- σ bonded ethylene is hydrogenated to an ethyl group followed by stepwise dehydrogenation of the α -carbon. We reject this mechanism because work on ethyl chloride by Lloyd et al. has shown that ethyl groups first dehydrogenate on Pt(111) to yield di- σ bonded ethylene rather than dehydrogenate directly to ethylidyne [28,29].

In the second mechanism a CH bond on the di- σ bonded ethylene breaks to form a vinyl group. This

vinyl group undergoes hydrogenation at the CH₂ carbon to form ethylidene. Ethylidene then dehydrogenates to form ethylidyne. This too can be ruled out on the basis of the vinyl iodide work by Zaera et al. which shows that vinyl decomposes readily to vinylidene and acetylene at temperatures around 140 K [21].

The last mechanism involves only two steps. First, a hydrogen atom undergoes a 1, 2 shift to form ethylidene. This is followed by a dehydrogenation step to form ethylidyne. Such a mechanism is consistent with experimental data and indeed involves the least number of steps. Therefore, in agreement with Carter and Koel we favor this last mechanism.

Clearly there is a third species present on Pt(111) during the dehydrogenation of di- σ bonded ethylene to ethylidyne. For the reasons stated above we believe that it is more likely that this species is ethylidene than ethyl, however, both species would show very similar spectral features in the CH stretch range. In addition, optical sum frequency generation has proven to be an excellent new technique for investigating the surface chemistry of this reaction.

5. Conclusion

Surface vibrational spectra of the transformation of di- σ bonded ethylene to ethylidyne have been recorded after each of eight annealing steps. The spectra show that in addition to the CH₃ and CH₂ symmetric stretch features from ethylidyne and di- σ bonded ethylene (respectively) there is a high frequency feature around 2957 cm⁻¹ during the transformation process. We have assigned this feature to the CH₃ asymmetric stretch of ethylidene and/or ethyl. Therefore, there is a third stable species present on the surface during the conversion of di- σ bonded ethylene to ethylidyne on Pt(111).

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