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The Direct Conversion of Vinyl to Ethylidyne

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The adsorption, desorption, and decomposition of vinyl iodide (C_2H_3I) on Pt(111) have been studied by temperature-programmed desorption (TPD), temperature-programmed second ion mass spectrometry (TPSIMS), x-ray photoelectron spectrometry (XPS), and high-resolution electron energy loss spectroscopy (HREELS). While the TPD data indicate that multilayer and monolayer of vinyl iodide desorb at 130 and 160 K, respectively, the XPS and HREELS data suggest that about 70% of vinyl iodide in the first layer dissociates into vinyl fragments and atomic iodine. While some vinyl exists up to 450 K, there are two important and competitive lower temperature reaction channels, and they lead to ethylidyne and ethylene.

In TPD, H_2 , C_2H_4 , C_2H_3I , and I are desorption products as shown in Figure 1. We assign the 130 K peak to physisorbed multilayers and the 160 K peak to chemisorbed monolayer C_2H_3I . H_2 desorbs mainly above 500 K, which is related to ethylidyne decomposition. The ethylene desorption implies a surface reaction, most likely the hydrogenation of vinyl species. Surface I, derived from C-I dissociation, desorbs atomically above 700 K.

To establish more clearly the connections between ethylene and vinyl iodide surface chemistry, we show in Figure 2 dihydrogen TPD spectra for

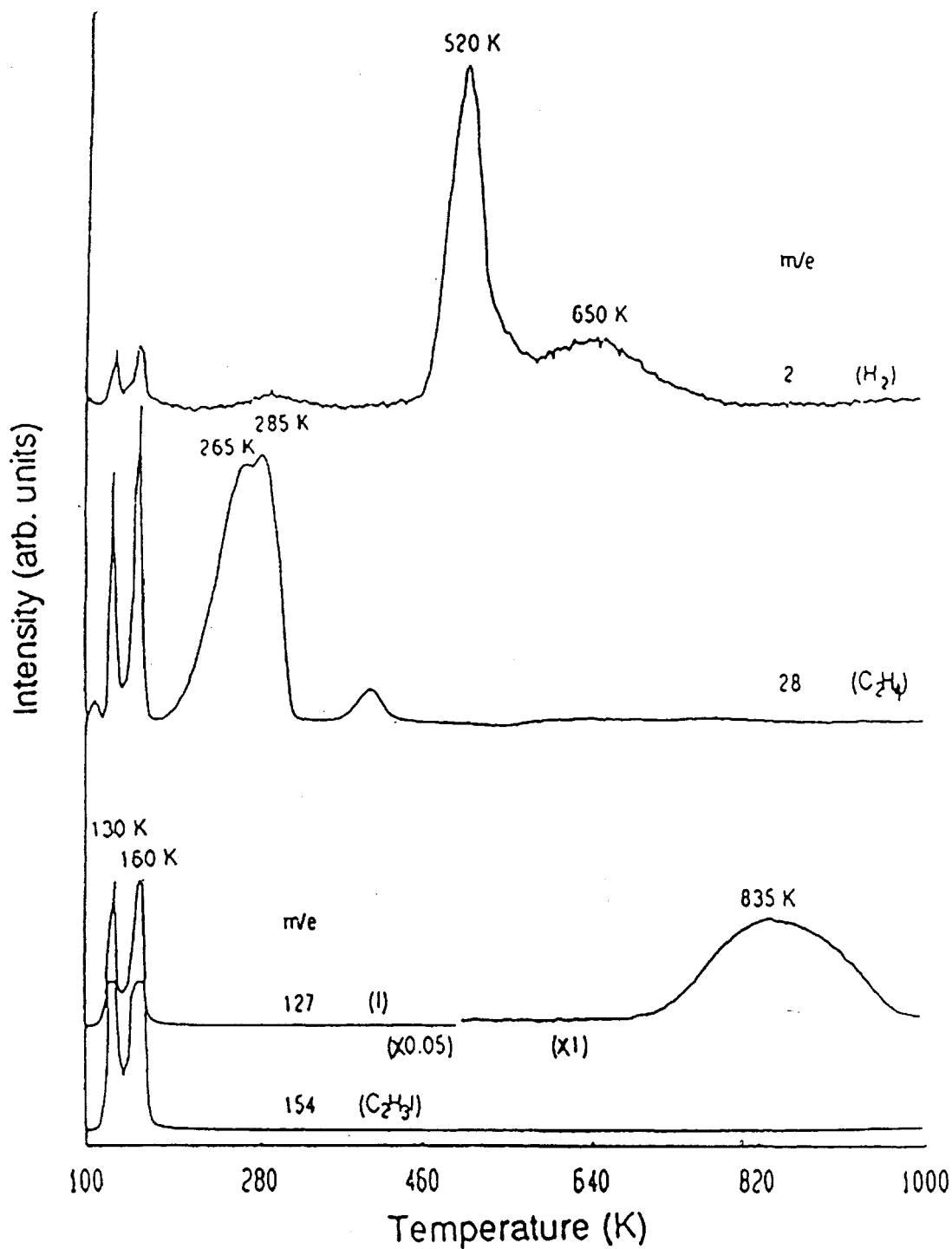


Figure 1 TPD spectra of mass 2, 28, 127, and 154 for a saturated $\text{C}_2\text{H}_3\text{I}$ exposure. The dosing temperature was 100 K and the heating rate was 6 K/s.

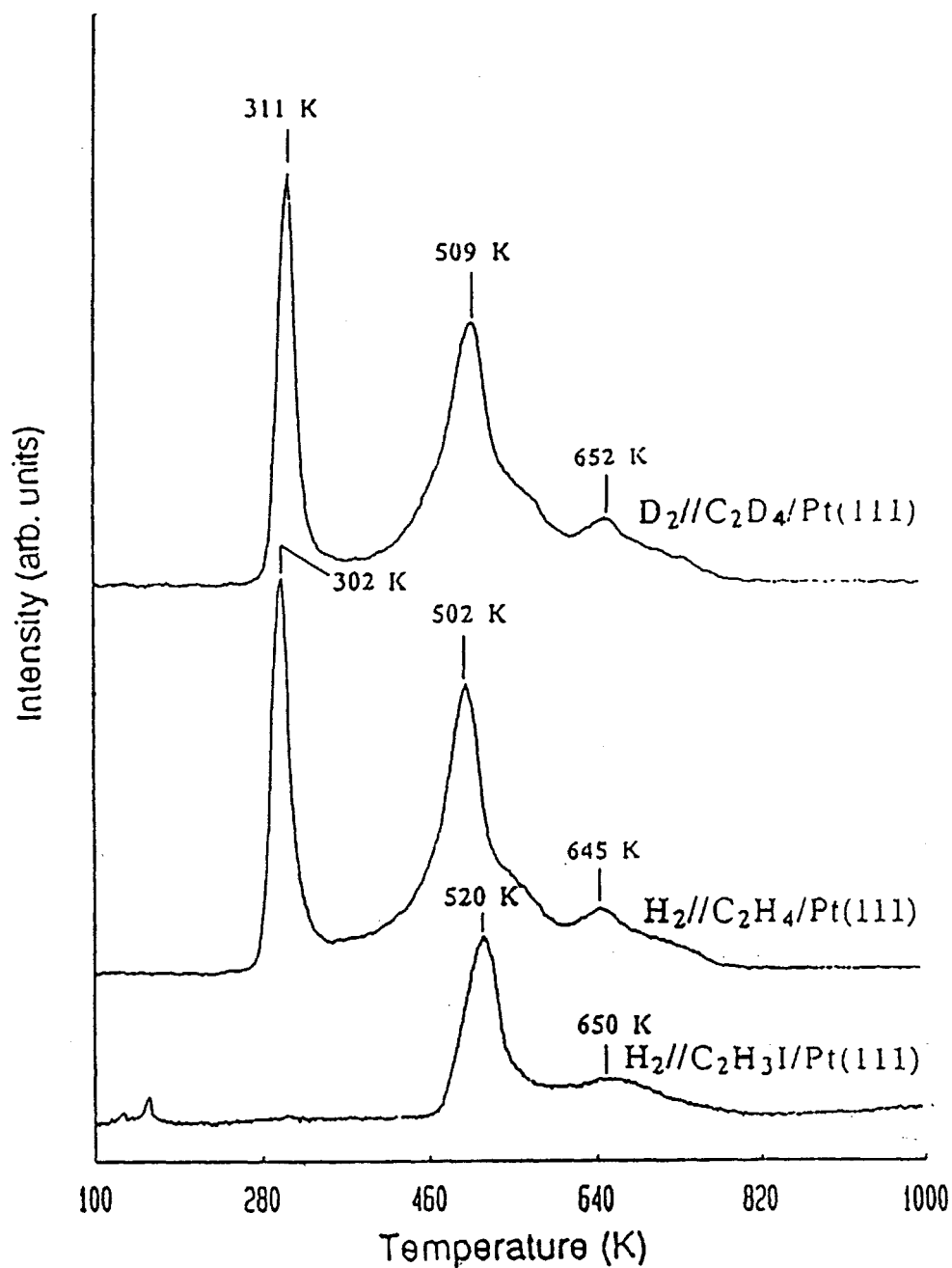


Figure 2 TPD spectra of dihydrogen for saturated monolayers of C_2H_4 , C_2D_4 , and C_2H_3I . The dosing temperature was 100 K and the heating rate was 6 K/s.

saturation monolayer doses of C_2H_3I , C_2H_4 , and C_2D_4 . In excellent agreement with earlier work [1–3], there are, for C_2H_4 , several discernible peaks at 302, 502, and 645 K and shoulders below and above 645 K. Only a small isotope effect, but nothing more, distinguishes the C_2D_4 case. For ethylene, it is well established that the lowest dihydrogen TPD peak is reaction-limited during the first C—H bond cleavage in the di- σ bonded ethylene, a dissociation accompanied by ethylidyne formation [1]. For C_2H_3I in Figure 2, this peak is absent, indicating that the reaction channel converting di- σ bonded ethylene to ethylidyne is blocked.

Previous work [1] shows that the CH_3^+ SIMS signal can be used to monitor the surface concentration of ethylidyne. Figure 3 summarizes methyl ion signals after dosing saturation amounts of C_2H_3I , C_2H_4 , and C_2D_4 ; the analogous TPD spectra are in Figure 2. For C_2H_4 and C_2D_4 , the CH_3^+ and CD_3^+ signals start to increase above 250 K (ethylidyne formation) and decrease above 400 K (ethylidyne decomposition), in agreement with earlier work [1]. There is a small isotope effect that favors the formation and decomposition of CCH_3 , consistent with the TPD results. For C_2H_3I , however, the CH_3^+ signal starts to increase as low as 120 K. After a plateau from 200 to 300 K, it increases again until it starts to decay above 450 K. The CH_3^+ signal from C_2H_3I is of particular interest; its high-temperature behavior tracks, just as for the ethylenes, the decomposition of ethylidyne. We take the low-temperature growth as evidence for facile vinyl conversion to ethylidyne directly without intervention of hydrogenation to ethylene. The increase between 300 and 450 K is taken to reflect the continuous formation of ethylidyne from vinyl, stabilized in the presence of high coverages of coadsorbed species. HREELS and XPS data also confirm the ethylidyne formation [4].

In summary, vinyl iodide adsorbs on Pt(111) both molecularly and dissociatively at 100 K. At high coverages, multilayer and monolayer of vinyl iodide desorb at 130 and 160 K, respectively. Upon heating, additional C—I bond cleavage occurs below the monolayer desorption temperature and, overall, about 70% of vinyl iodide in the first layer dissociates. There are two competitive reaction channels for vinyl species:

- (a) $—CH=CH_2 \rightarrow —CCH_3$
- (b) $—CH=CH_2 \rightarrow —CH_2H_2C—$

Vinyl conversion to ethylidyne, reaction (a), starts at 120 K, but in the presence of large amounts of I, here is evidence that some vinyl fragments are stable up to 450 K. Reaction (b) is enhanced when surface hydrogen is available, as it is when deuterium is preadsorbed or when intermediate coverages of parent allow C—H cleavage at low temperature. The ethylene

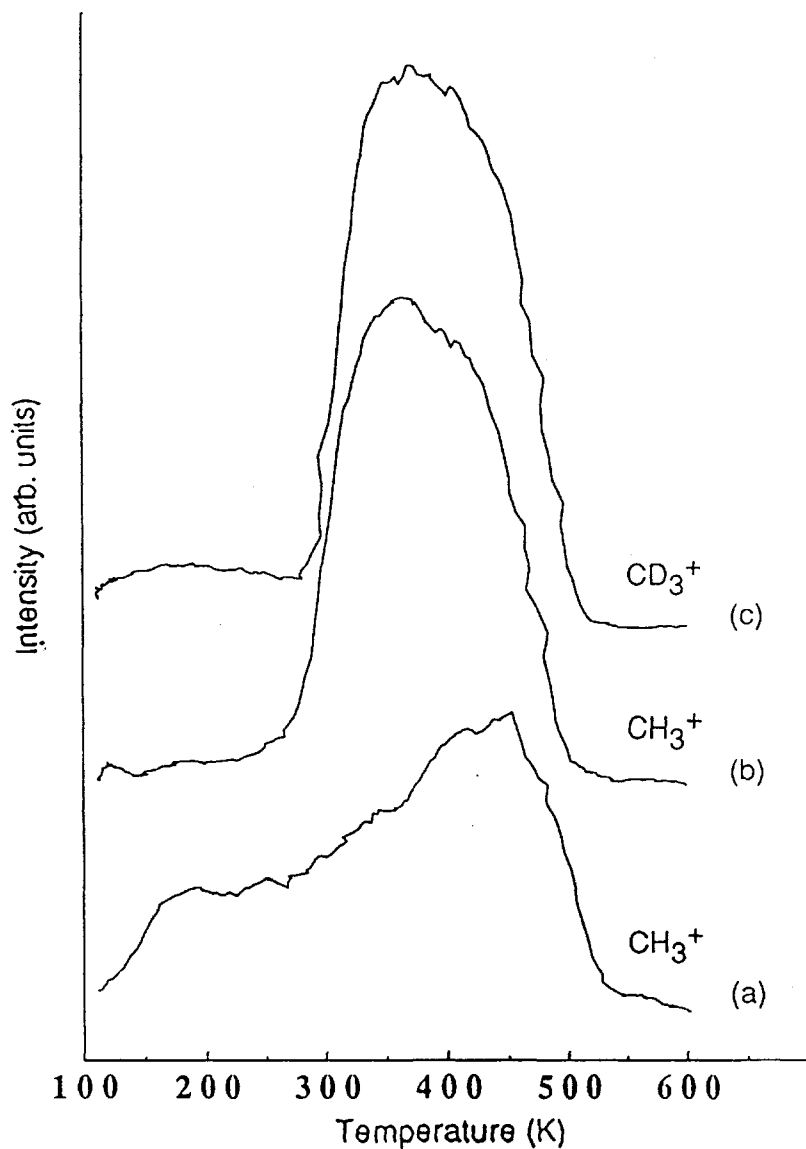


Figure 3 TPSIMS spectra of methyl ions from surfaces saturated with monolayers of $\text{C}_2\text{H}_3\text{I}$ (a), C_2H_4 (b), and C_2D_4 (c). The dosing temperature was 100 K and the heating rate was 6 K/s.

desorption from C_2H_3I is reaction-limited and occurs at a lower temperature than for ethylene chemisorbed alone on Pt(111).

The results suggest that the first C—H bond cleavage is the rate-determining step for ethynidyne formation from ethylene on Pt(111) and that vinyl is a facile intermediate in the conversion of ethylene to ethynidyne.

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