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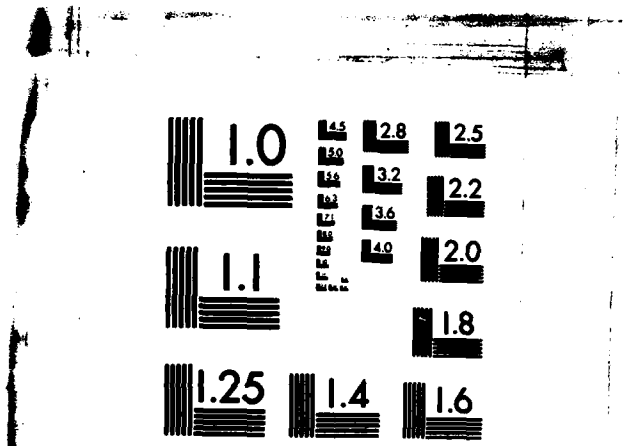

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The thermal decomposition of acetylene (C_2H_2) on palladium (100) and (111) surfaces in the temperature range 300-500K has been monitored with high-resolution electron energy loss spectroscopy (EELS). Vibrational analysis indicates predominant formation of rather stable CCH species on both surfaces.

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Technical Report No. 9

ACETYLENE DECOMPOSITION ON Pd(100) AND Pd(111): EELS EVIDENCE FOR CCH FORMATION

by

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Bloomington, Indiana 47405

16 January 1984

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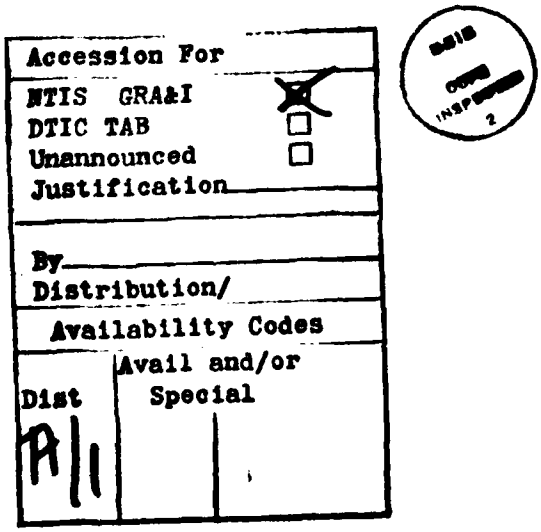

SUMMARY ABSTRACT: ACETYLENE DECOMPOSITION ON Pd(100) and Pd(111): EELS EVIDENCE FOR CCH FORMATION

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Acetylene chemistry on palladium surfaces appears to be a complex and fascinating topic. Several recent ultraviolet photoemission (UPS) and thermal desorption (TDS) spectroscopic studies, for example, have indicated the formation of both benzene (C_6H_6) and ethylene (C_4H_4) on certain low index crystal faces of the material.[1-3] Sesselmann et al. have reported C_6H_6 formation on Pd(111) under conditions of low temperature and high exposure ($\gtrsim$ 100L) using TDS and UPS.[1] However, Tysoe et al. (UPS, TDS)[2] and Gentle and Muetterties[3] (TDS) detected reactively-formed C_6H_6 at both low (230K) and high (500K) temperatures on Pd(111). The latter group also found evidence for the trimerization reaction on Pd(100) and Pd(110) but the reaction was reportedly more extensive on Pd(111).[3] The above studies complement the earlier investigations of Gates and Kesmodel[4] where CCH_2, CCH_3, and CH formation were reported from C_2H_2 thermal evolution on Pd(111) using vibrational analysis with high-resolution electron energy loss spectroscopy (EELS).

In view of the diversity of the above results concerning C_2H_2 low pressure surface chemistry on Pd surfaces we have undertaken more extensive EELS studies on both Pd(100) and Pd(111). A central issue we have addressed is the possible detection of reactively-formed C_6H_6 in the temperature range 300-500K. In this summary abstract we note the salient results

of this study. A complete discussion of this investigation will be presented elsewhere.[5] We find C_2H_2 decomposition on both Pd(100) and Pd(111) is dominated by the formation of rather stable CCH species which persist to ~550K before additional dehydrogenation occurs. The chemistry on the (111) and (100) surfaces may be distinguished: On Pd(111) the formation of both CCH and ethylidyne ($\equiv C-CH_3$) occurs upon 300K C_2H_2 adsorption (with decomposition of ethylidyne near 450K). On Pd(100) C_2H_2 adsorbs associatively at 300K and forms CCH near 400K. No direct vibrational spectroscopic evidence for benzene formation was found in the present study.

The high-resolution EELS measurements were carried out with two 127° cylindrical deflection electron spectrometers. The Pd(111) experiments were performed with a single-pass instrument[6] which is housed in an ion-pumped ultrahigh vacuum system (base pressure ~1 x 10^{-10} Torr). This instrument was operated at 10 meV (80 cm^{-1}) system resolution at typical elastic beam signal levels of 0.3-1.0 x 10^5 cps for hydrocarbon adsorption. The Pd(100) experiments employed a new double-pass spectrometer which achieves high signal levels at 2.5-10 meV system resolution.[7] This instrument is incorporated in a diffusion/sublimation-pumped system (base pressure ~5 x 10^{-11} Torr). Due to the generally low intensity of the hydrocarbon modes the spectrometer was operated at 8-9 meV (64-72 cm^{-1}) system resolution at typical elastic beam count rates of 2 x 10^6 cps. Sample preparation and cleaning have been described elsewhere.[4]

A summary of basic EELS experiments carried out on both

(111) and (100) surfaces is listed below. Unless noted otherwise the spectra were obtained under specular scattering conditions: (1) C_2H_2 (C_2D_2) adsorption (300K) and thermal processing (300-600K); (2) C_6H_6 (C_6D_6) adsorption (300K) and thermal processing (300-600K); (3) Off-specular EELS comparison of acetylene-derived surface species (450-475K) and benzene (Pd(100) only); (4) $C_2H_2 + C_2D_2$ isotope mixing (300-500K); (5) $C_6H_6 + D_2$; $C_6D_6 + H_2$ isotope mixing (150-500K) (Pd(111) only).

In the course of these studies it was found that the surface species which remains after annealing 300K chemisorbed C_2H_2 to 450K exhibited major vibrational features similar to C_6H_6. Representative spectra for Pd(100) to illustrate this aspect are shown in Fig. 1. Spectrum 1(a) is due to associatively chemisorbed acetylene. Spectra 1(b) and 1(c) both exhibit strong CH bending losses ca. 730-750 cm^{-1} and weak CH stretching losses ca. 3000-3020 cm^{-1}. However, detailed comparison of the weaker losses, including off-specular analysis, clearly differentiates between the 450K C_2H_2-derived species and chemisorbed C_6H_6. Particularly conclusive were the isotope-mixing experiments noted above which favored a CH or CCH species. The presence of a CC stretching mode ca. 1340 cm^{-1} in both C_2H_2 and C_2D_2 derived species rules against CH and leaves CCH as the most probable interpretation of the spectra. The carbon-carbon bond order deduced from the CC and CH stretching frequencies is between 1 and 2, indicating that both carbon atoms are involved in the CCH interaction with the metal surface.

I thank Dr. J.E. Demuth for numerous stimulating

discussions. This work was supported by the Office of Naval Research.

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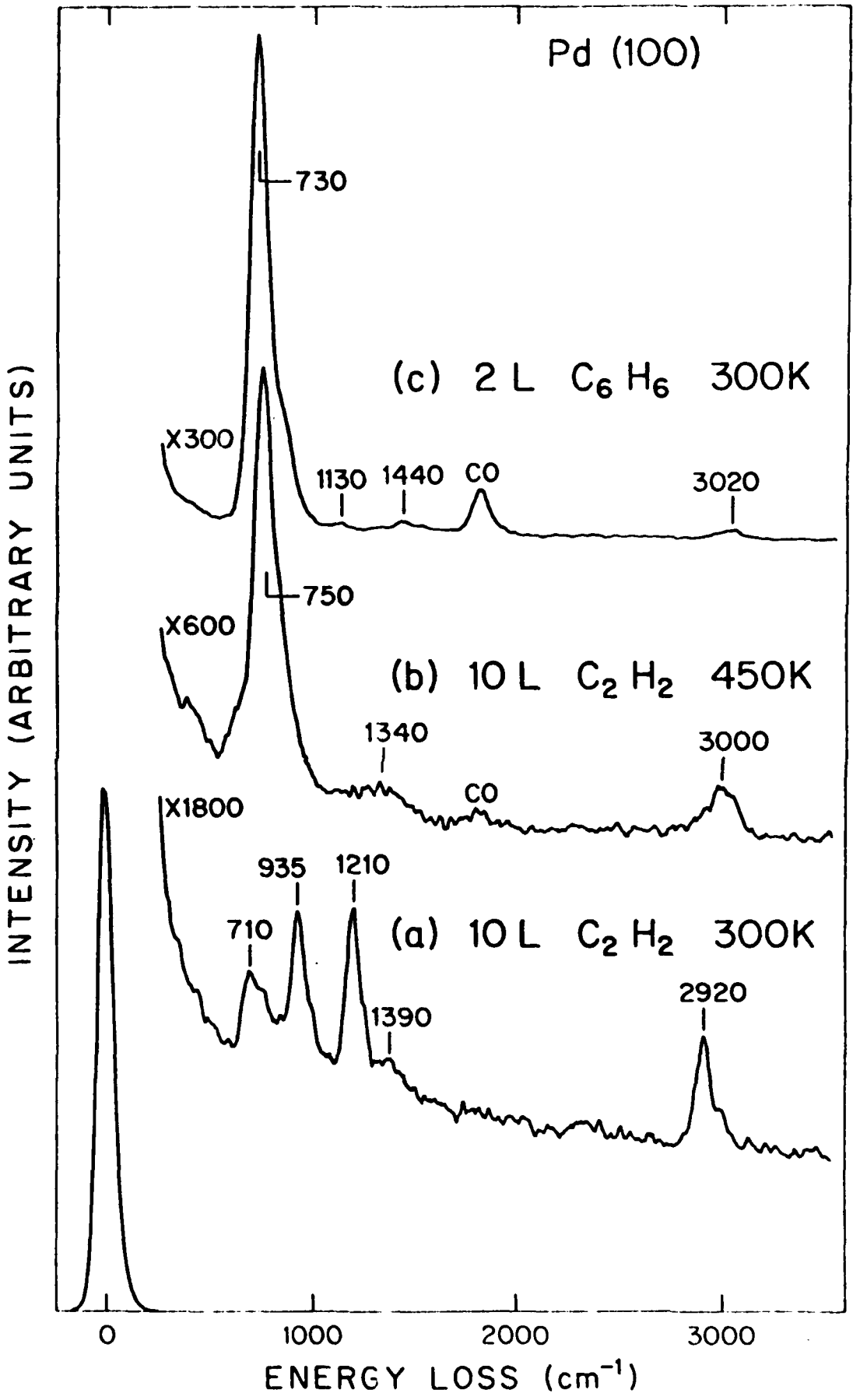
Figure Caption

Fig. 1: High-resolution EELS spectra for hydrocarbon adsorption on Pd(100).


Pd (100)
730
(c) 2 L C6 H6 300K
X300
1130
1440
CO
3020
750
X600
(b) 10 L C2 H2 450K
1340
3000
CO
X1800
935
1210
710
(a) 10 L C2 H2 300K
2920
1390
INTENSITY (ARBITRARY UNITS)
0
1000
2000
3000
ENERGY LOSS (cm-1)