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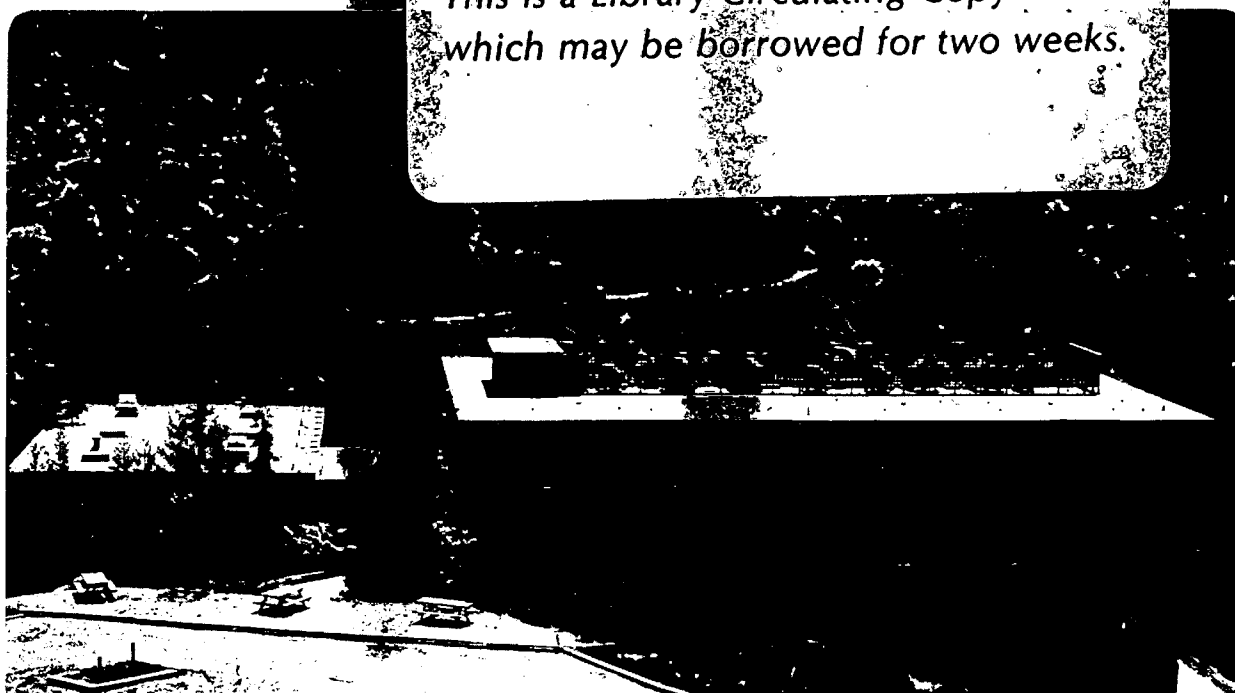## Materials & Molecular Research Division

HYDROGENATION OF CHEMISORBED ETHYLENE ON CLEAN,
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CRYSTAL SURFACES

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HYDROGENATION OF CHEMISORBED ETHYLENE ON CLEAN, HYDROGEN, AND ETHYLIDYNE COVERED PLATINUM (111) CRYSTAL SURFACES

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Abstract

The hydrogenation of chemisorbed ethylene was examined on platinum (111) single crystals under ultra-high vaccuum using temperature programmed desorption. Ethane was formed in a self-hydrogenation process with an activation energy of 18 kcal/mole, while in the presence of preadsorbed hydrogen, ethane was formed with an activation energy of 6 kcal/mole. A mechanism is proposed for the low pressure hydrogenation which is supported by a computer simulation.

At temperatures below 320 K, an ethylidyne saturated Pt (111) surface requires hydrogen pressures greater than 10^{-5} torr for coadsorption. Ethylene binds to this surface very weakly or not at all, and consequently no ethane was observed to desorb from this surface during TPD.

The results obtained support the model of direct participation of a carbonaceous layer during the steady state catalytic hydrogenation of ethylene on platinum (111) at atmospheric pressures and room temperature, as previously reported.

INTRODUCTION

The adsorption of ethylene on platinum (111) has been extensively studied from 77 K to above 500 K [1,2,3,4,5]. Using temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS), different adsorption states have been identified in different temperature regions [1,2,3]. Below 290 K ethylene chemisorbs molecularly to platinum (111) and lies parallel to the surface with a carbon-carbon bond length of 1.49 Å [4]. Around room temperature a hydrogen atom is lost to the surface with a subsequent C-H bond shift so that the remaining hydrogen atoms are all bonded to one of the carbon atoms. The resulting ethylidyne species (CCH_3), as identified through LEED I-V analysis [5], stands perpendicular to the surface in a three fold hollow, the α carbon atom being bonded to three platinum atoms with a carbon-carbon bond length of 1.50 Å . Above 450 K additional hydrogen atoms are lost, forming first hydrocarbon fragments of the stoichiometry C_xH where x is between 1 and 2, followed by total dehydrogenation and graphite formation at higher temperatures.

The adsorbed state of ethylene on platinum (and other metals) at room temperature is particularly important because of the role it plays during the catalytic hydrogenation of ethylene. It has been proposed recently [6] that the steady state catalytic hydrogenation of ethylene over Pt (111) at atmospheric pressures and at 300 K occurs not on the bare metal surface, but on top of a tenaciously adsorbed ethylidyne layer. This model is supported by the following results: i) the hydrogenation rate of ethylidyne is much slower than that of ethylene near room temperature; ii) a Pt (111) surface saturated with ethylidyne yields the same kinetic parameters for this reaction as does a clean surface; iii) ethylidyne is also present at the completion of a high

pressure (~ atmospheric) reaction when the crystal is returned to ultra-high vacuum (UHV). However, the state of the surface during the high pressure hydrogenation is not known.

Since it is difficult to probe the surface at pressures larger than 10^{-5} torr using most surface science techniques, this work was undertaken to gather information relating to the hydrogenation of adsorbed ethylene over Pt (111) using temperature programmed desorption (TPD) under UHV. It was found that ethylene could be hydrogenated to ethane in low yields in the absence of hydrogen during TPD in a self-hydrogenation process. The ratio of desorbing ethane to ethylene increased when hydrogen was pre-adsorbed on the surface. A mechanism was proposed for the ethylene self-hydrogenation and the surface reaction between preadsorbed hydrogen and ethylene under UHV, and it was tested by a computer simulation using the kinetic parameters determined from this work and elsewhere. The coadsorption of ethylidyne and hydrogen under different hydrogen pressures was also examined, and evidence was found suggesting the formation of ethylidene ($CHCH_3$) at higher hydrogen pressures. These results further support the model previously proposed where the steady state catalytic hydrogenation of ethylene occurs on top of an ethylidyne/ethylidene overlayer and not over the bare metal surface [6,7,8,9].

EXPERIMENTAL

Temperature programmed desorption experiments were performed in a stainless steel UHV system pumped with a liquid nitrogen trapped diffusion pump, the base pressures obtained were less than 10^{-9} torr. The system was equipped with a four grid retarding field analyzer used for low energy

electron diffraction (LEED) and Auger electron spectoscopy (AES), an ion gun for argon ion sputtering, a quadrupole mass spectrometer, and a retractable internal isolation cell for high pressure work (~ 1 atm). Platinum single crystals (99.995% purity) were cut to within 1° of the (111) orientation and both faces were polished. The area of the disks obtained was about 1 cm^2 and the thickness was < 0.5 mm. The crystals were spot-welded to platinum wires (0.020 in.) which in turn were spot-welded to gold wire supports afixed to a liquid nitrogen cooled copper block at the base of the manipulator. Resistive heating was used and the temperature monitored using a chromel/ alumel thermocouple spot-welded to the edge of the crystal. The area due to the platinum support wires and crystal edges was less than 30%. A clean crystal was obtained by cycles of heating in oxygen followed by argon ion sputtering at 700°C and annealing at 1000°C until no impurities (mainly S,C,Ca,O) could be detected using AES. Research purity ethylene (Matheson 99.98% purity), hydrogen (Matheson 99.99% purity), and deuterium (Matheson > 99.5% atomic purity) were used as supplied.

Hydrogen and ethylene were dosed at $5x10^{-7}$ and $2x10^{-8}$ torr respectively and at 150 K unless otherwise specified. Pressures reported were not corrected for ion gauge sensitivity. Ethylidyne covered surfaces were prepared by holding the crystal temperature at 325 K while dosing with ethylene. Temperature programmed desorption was always performed after allowing the crystal to cool to 150 K using a heating rate of 30 K/sec. Dosing of hydrogen at atmospheric pressures was accomplished using a retractable internal isolation cell, as described in detail elsewhere [10]. The crystal temperature always increased to ~ 250 K while exposing to one atmosphere of hydrogen, even with liquid nitrogen cooling.

RESULTS

Self-Hydrogenation of Ethylene on Pt (111)

Ethylene adsorbs molecularly on platinum at 150 K [1,2,4], and during TPD the desorption of H_2, C_2H_4, and C_2H_6 were observed (fig. 1). The mole ratio of desorbing C_2H_6, H_2, and C_2H_4 was 1:20:50. The formation of methane and C_4 products was not detected.

Ethane was produced from ethylene on platinum (111) in a self-hydrogenation process. To prove that background hydrogen was not participating in the hydrogenation, TPD experiments were carried out using an ethylene saturated surface while keeping a background pressure of 10^{-6} torr deuterium. The intensity and temperature of the desorption maximum of the 30 amu. peak was the same whether or not D_2 was present, and no deuterated ethanes (31 and 32 amu.) were observed.

The temperature of the desorption maximum (T_{max}) of ethane for the self-hydrogenation process was found to be 302 K and independent of the initial ethylene coverage indicating first order kinetics. Following an induction period below 0.4 Langmuirs (L, 1 L = 10^{-6} torr-sec.) of ethylene, the ethane yield increased almost linearly with respect to ethylene exposure until 1.1 L at which point saturation occurs (fig. 2).

Desorption activation energies were calculated from TPD using the method of Chan et. al. [11]. The desorption of H_2, C_2H_4, and C_2H_6 were all found to be first order in ethylene coverage, and the values obtained in units of kcal/mole were: 17 ± 3 for the first H_2 evolution peak, 9 ± 2 for for ethylene molecular desorption, and 18 ± 4 for ethane formation (table I). The values obtained for hydrogen and ethylene desorption are in agree-

ment with those obtained by Salmeron and Somorjai [2].

Hydrogenation of Ethylene over the Hydrogen Predosed Pt (111) Surface

The presence of ethylene on the platinum surface inhibited the coadsorption of hydrogen. However, when the surface was predosed with hydrogen or deuterium, ethylene coadsorption did take place and ethane formation was enhanced. TPD taken after predosing the surface with 25 L of hydrogen followed by 0.4 L of ethylene gave an ethane peak centered at 252 K and much broader than in the self-hydrogenation case (table I and fig. 3). The mole ratio of desorbing ethylene to ethane decreased with increasing coverage of preadsorbed hydrogen from 50 for self-hydrogenation to near unity with 25 L of predosed hydrogen. This was qualitatively in agreement with results recently reported by Berlowitz et. al. [12]. When the surface was predosed with deuterium all deuterated ethanes, including d_6 ethane, were detected indicating that considerable exchange occured on the ethane precursors. A rigorous calculation of the ethane product distribution was complicated by the simultaneous exchange occuring on ethylene. The TPD data recorded in the 30-36 amu. range were deconvoluted (fig. 4), but precise values for ethanes below d_2 were not possible to obtain and only upper limits are reported.

The coverage dependence for ethane production on hydrogen and ethylene was examined. Predosing the surface with varying exposures of hydrogen followed by an ethylene exposure of 0.4 L gave an increase in ethane production and a decrease in T_{max} with increasing hydrogen exposure (figs. 3,5). Exposing the surface to 30 L of hydrogen followed by varying exposures of ethylene also gave an increase in ethane production and a decrea-

sing T_{max} with increasing ethylene exposure (fig. 6). Interestingly, the temperature of the desorption maximum reached a minimum of ~ 250 K near a 1 L exposure of ethylene and remained near 250 K while the C_2H_6 desorption area continued to increase even at ethylene exposures of 20 L.

Ethylene and Hydrogen Coadsorption in the Presence of Ethylidyne on Pt (111)

Ethylene chemisorption at room temperature forms ethylidyne on the surface [5]. Once the surface is saturated with ethylidyne, no further ethylene will adsorb at either UHV or high pressure conditions. TPD experiments following exposures of ethylidyne saturated platinum to $1-10^8$ L of ethylene from 150 to 320 K showed no production of ethane or molecular desorption of ethylene.

The ability of the Pt (111) surface to adsorb hydrogen in the presence of ethylidyne was also examined. The H_2 TPD of an ethylidyne saturated surface was obtained (fig. 7a). The same spectrum was obtained when hydrogen coadsorption was attempted at 150 K under UHV, suggesting that no hydrogen adsorption takes place under these conditions. However, hydrogen could be coadsorbed at $5x10^{-7}$ torr when a sub-saturation coverage of ethylidyne was present on the platinum surface (fig. 7, b&c). An H_2 TPD from clean platinum was recorded for reference (fig. 7d). Saturation of the surface with respect to ethylidyne occured at ethylene exposures near 1.6 L (fig. 8).

Hydrogen could be adsorbed on an ethylidyne saturated surface when higher hydrogen pressures were used. For example, when an ethylidyne saturated surface was exposed to one atmosphere of hydrogen for one minute (~ 10^{10} L), the H_2 TPD displayed an additional low temperature peak near 270 K (fig. 9d). This peak was most likely due to hydrogen desorbing

directly from the platinum surface. Experiments performed with deuterium indicated that no deuterium exchange occured on the methyl group, and only the low temperature peak was seen in the deuterium TPD (fig. 9e) Ethylidyne hydrogenation is very slow at these temperatures [7], and was not observed during these experiments.
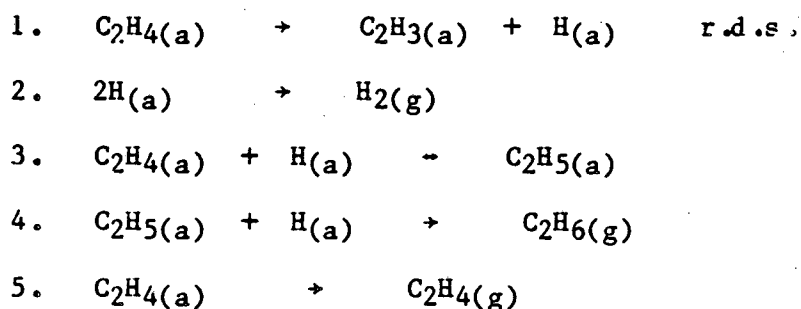
It was also found that hydrogen could be coadsorbed on an ethylidyne saturated surface at pressures as low as 10^{-5} torr. The hydrogen adsorption state observed depended on the temperature of coadsorption (fig. 9, b&c). When hydrogen was dosed at 150 K, H_2 desorption peaks were observed at 219 and 298 K corresponding to desorption from platinum metal (fig. 9b). When hydrogen was dosed at 320 K followed by immediate cooling of the crystal to 150 K, an H_2 desorption peak was observed at 385 K (fig. 9c). The hydrogen adsorption state corresponding to the 385 K desorption peak was found to decay rapidly at 320 K, and significant decay was observed even at 150 K after 10 minutes. Pressures significantly lower than 10^{-5} torr (ie. 10^{-6} torr) were ineffective in producing the above hydrogen adsorption states on ethylidyne saturated platinum.

DISCUSSION

Model for the UHV Hydrogenation of Chemisorbed Ethylene on Clean and Hydrogen Predosed Platinum

Ethylene decomposition on Pt (111) surfaces has been extensively studied [1,2]. The peaks at 320 and 530 K in the H_2 TPD of ethylene correspond to the conversion of adsorbed C_2H_4 to ethylidyne and to the decomposition of ethylidyne respectively. Ethane is among the thermal

desorption products of ethylene, a product of self-hydrogenation. Self-hydrogenation of ethylene has been observed previously on Pt, Rh, Ir, Ni, Pd, and W [1,13-18]. During the decomposition of adsorbed ethylene to ethylidyne on platinum, hydrogen atoms are spilled onto the surface. These hydrogen atoms are then able to hydrogenate other adsorbed ethylene molecules to ethane which then desorb. The rate determining step (r.d.s.) for this process is the breaking of a C-H bond, which is responsible for the first order dependence on ethylene coverage for ethane formation at 302 K, and H_2 desorption at 320 K. Additionally, activation energies calculated for both processes were equivalent within experimental error (18 ± 4 kcal/mole for C_2H_6 formation and 17 ± 3 kcal/mole for H_2 evolution). When hydrogen is coadsorbed with ethylene (as was the case for the predosing experiments), the hydrogenation proceeds directly without involving any C-H bond breaking. This is why the ethane peak became broader and shifted from 300 K for very low hydrogen exposures to 250 K for larger exposures. Based on these observations we propose the following mechanism for the self-hydrogenation:

1. $C_2H_4(a)$ $\rightarrow$ $C_2H_3(a)$ $+$ $H(a)$ r.d.s.

2. $2H(a)$ $\rightarrow$ $H_2(g)$

3. $C_2H_4(a)$ $+$ $H(a)$ $\rightarrow$ $C_2H_5(a)$

4. $C_2H_5(a)$ $+$ $H(a)$ $\rightarrow$ $C_2H_6(g)$

5. $C_2H_4(a)$ $\rightarrow$ $C_2H_4(g)$

A computer simulation of the preceeding model was developed using the kinetic parameters determined from this work and elsewhere (table II). The kinetic parameters for step 1 were extracted from the first hydrogen desorption peak which was due the to decomposition of ethylene to ethylidyne. This is so because once hydrogen is formed on the surface

due to the breaking of C-H bonds, the temperature is high enough so that the recombination and desorption of H_2 is fast. The parameters used were: $E_a = 17$ kcal/ mole and $\nu = 4 \times 10^{13}$. The activation energy was taken from this work and the preexponential factor was taken from the paper by Salmeron and Somorjai [2].

The desorption parameters of H_2 from Pt (111) were taken from the work of Christmann et. al [19]. The parameters used for step 2 were $E_a = 9$ kcal/mole and $\nu = 0.075$ for the second order process. Molecular desorption of ethylene was observed and the kinetic parameters used were taken from Salmeron and Somorjai [2]. They were: $E_a = 9$ kcal/mole and $\nu = 9.2 \times 10^6$.

The kinetic parameters for steps 3 and 4 were not easily accessible. If the hydrogenation were to take place in a concerted way, the overall rate expression for the two hydrogenation steps combined would be:

$$\text{rate} = \theta^2_H \, \theta_{C_2H_4} \, \nu \exp(-E_a/RT)$$

This expression is third order overall, second order in hydrogen and first order in ethylene. However, it is likely that the hydrogenation occurs in two successive steps, one of which is rate determining, and each of which is first order in hydrogen and second order overall. The coverages of hydrogen and ethylene for step 3 and the coverages of hydrogen and the surface ethyl radical for step 4 change with time (and temperature) in an undetermined way. For this reason it may not be possible to use the well established methods of determining kinetic parameters from the TPD for the hydrogen predosed system (fig. 3). This leaves four undetermined parameters to be fixed in order to get good agreement with the experimental data.

A considerable amount of C_2D_6 desorbed during TPD (fig. 4) when D_2

and C_2H_4 were coadsorbed on the platinum (111) surface. This can be ex-plained if a fast equilibrium is attained between adsorbed ethylene and the surface ethyl radical, and if the second hydrogenation step is rate limiting for the formation of ethane. The method of Chan et. al. [11] for a second order desorption was used as a first approximation and an activation energy of 6 ± 1 kcal/mole was calculated for the thermal de-sorption processes shown in figure 3. This activation energy was assigned to step 4, the second and rate limiting hydrogenation step.

The first hydrogenation step and its reverse were assumed to be fas-ter than the second hydrogenation step. This leads to deuterium exchange as below:

$$C_2H_{4(a)} + D_{(a)} \leftrightarrow C_2H_4D_{(a)} \leftrightarrow C_2H_3D_{(a)} + H_{(a)}$$

Furthermore, adsorbed C_2H_4 and C_2H_5 are proposed to be in dynamic equi-librium, then:

$$K_{eq} = \theta_{C_2H_5} / \theta_{C_2H_4} \theta_H = k_3/k_{-3} = (\nu_3/\nu_{-3})\exp[(E_{-3}-E_3)/RT]$$

The following three parameters were selected for use in the model:

$$(\nu_3/\nu_{-3}) = 0.03 \; ; \; (E_{-3}-E_3) = 2 \text{ kcal/mole} \; ; \; \nu_4 = 1.47 \times 10^{-3}$$

The surface hydrogenation model is summarized in table II, and computer generated results accompany the experimental results in figures 1, 2, 3, 5, and 6. They were in excellent agreement with experiment for both the self-hydrogenation and hydrogen coverage dependence for the hydrogen pre-adsorbed system.

Additional calculations were performed in order to justify the selec-tion of the kinetic parameters for the hydrogenation steps. Keeping all other parameters the same, the activation energy for step 4, the final hydrogenation step, was adjusted with its corresponding preexponential factor so that the ethane yield during self-hydrogenation of ethylene

remained unchanged. The position of T_{max} and the full width at half maximum (FWHM) for ethane desorption were computed as a function of the activation energy (E_4) for ethylene hydrogenation when a large coverage of preadsorbed hydrogen was present. Experimentally, T_{max} was 250 K and the FWHM was 65 K under these conditions (30 L H_2 predose). The model gave the best agreement with experiment (T_{max} and FWHM) when E_4 was 6 kcal/mole. As E_4 was increased, T_{max} increased and the FWHM decreased. At E_4 = 9 kcal/mole, T_{max} was 265 K and the FWHM was too narrow at 45 K. On the other hand, as E_4 was decreased, T_{max} decreased rapidly and was 200 K at E_4 = 3 kcal/mole.

Ethylene and Hydrogen Coadsorption in the Presence of Ethylidyne

Zaera and Somorjai [6] have recently reported that a saturation layer of ethylidyne was formed immediately and irreversibly on the platinum (111) surface during the high pressure (~ 200 torr) steady state catalytic hydrogenation of ethylene. Ethylidyne is stable under atmospheric pressures of hydrogen and at room temperature since the hydrogenation and exchange of deuterium for hydrogen on the methyl group is much slower (~ 10^{-3} times slower) than the catalytic hydrogenation of ethylene [7,8,9]. Ethylidyne was always found on the Pt (111) crystal upon return to UHV conditions following a hydrogenation reaction. Also, restart reactions on ethylidyne covered platinum gave the same rates of reaction as for clean surfaces. All of the above suggest direct participation of the carbonaceous overlayer during the steady state hydrogenation of ethylene at atmospheric pressure and near room temperature. We propose that after dihydrogen dissociates on the platinum surface, the hydrogen atoms are transfered indirectly from the platinum surface to weakly bound ethylene molecules

through the α carbon of the ethylidyne species, via the formation of ethylidene ($CHCH_3$) intermediates (fig. 10).

In support of this scheme it has been demonstrated that hydrogen could be adsorbed on an ethylidyne saturated platinum surface when the pressure was greater than 10^{-5} torr at temperatures between 150-320 K. The amount of hydrogen that could be adsorbed on this surface with a one atmosphere exposure ($\sim 10^{10}$ L) was about 25% the amount that could be adsorbed on a clean platinum (111) surface with a 30 L exposure.

At pressures around 10^{-5} torr detectable quantities of hydrogen could also be adsorbed on the ethylidyne saturated surface between 150-320 K, but equivalent exposures at $< 10^{-6}$ torr gave no detectable hydrogen adsorption. Competition between adsorption and desorption produced a steady state surface concentration of hydrogen. Larger coverages were obtained with higher hydrogen pressures until saturation was reached. Two different hydrogen states were seen in the TPD depending on the adsorption temperature. The H_2 desorption peaks around 290 K (fig. 9b) were probably due to hydrogen desorbing from the platinum surface while the 385 K (fig. 9c) desorption peak was possibly related to a hydrocarbon decomposition. The presence of the 385 K peak suggests the existence of ethylidene ($CHCH_3$) on Pt (111) when higher hydrogen pressures were applied to an ethylidyne saturated surface. The peak was found on the low temperature side of the ethylidyne decomposition peak, consistent with calculations of Kang and Anderson [20] which predict that ethylidene is less stable than ethylidyne at low hydrogen pressures. A high steady state concentration of ethylidene would be favored by high hydrogen pressures. Under UHV, however, the ethylidene – ethylidyne equilibrium would be completely shifted towards the more dehydrogenated moiety. Therefore, the ethyli-

dene decomposition product is probably ethylidyne, and within experimental error, the area and shape of the hydrogen desorption peak from ethylidene above 420 K was no different than the area and shape of a typical ethylidyne desorption spectrum (fig. 9).

The Steady State Catalytic Hydrogenation of Ethylene over Platinum

These results have implications for the catalytic hydrogenation of ethylene. First, if ethylene was hydrogenated directly on the platinum surface, an activation energy of 6 kcal/mole would be observed instead of 8-15 kcal/mole as reported elsewhere [6,21-26]. Extrapolating the surface hydrogenation model proposed here (table II) to steady state conditions and moderate pressures gave a rate expression very different than that determined by Zaera and Somorjai [6] for ethylene and hydrogen on platinum (111). Also, the ethane deuterium distribution obtained from D_2 + C_2H_4 experiments under UHV (fig. 4) was much different from that obtained for high pressure deuteration [6].

There have been observations made in the literature that support the proposed direct participation of carbonaceous deposits during the catalytic hydrogenation of ethylene on metallic surfaces. Laidler and Townsend [27] reported two activation energies for ethylene hydrogenation over Ni films (7.8 and 10 kcal/mole) depending on whether hydrogen or ethylene was introduced into the reactor first. When hydrogen was introduced first, the fast initial rate gave way to the slower rate obtained when ethylene was introduced first, indicating that as surface hydrogen was depleted, surface metal metal atoms became available for the adsorption of hydrocarbon which forms stronger bonds to the surface than does hydrogen. Similar rate dependences

have been seen for other systems [17].

The possibility exists that on the platinum (111) surface, the catalytic hydrogenation still proceeds directly on the metal surface, but a larger activation energy is observed because ethylidyne hinders the approach of ethylene to the surface. Although this explanation cannot be discarded, it seems unlikely since neither ethylene nor ethane were found to desorb when attempts were made to adsorb ethylene on an ethylidyne saturated surface, even at atmospheric pressure.

Finally, Wieckowski et. al. [28] reported an activation energy of 5.9 kcal/ mole for the hydrogenation of ethylene over platinum (111) in solution where H^+ was reduced at the surface giving surface hydrogen. They propose that ethylene is hydrogenated directly on the clean platinum surface, similar to the process of surface hydrogenation observed under UHV in our experiments.

CONCLUSIONS

The hydrogenation of chemisorbed ethylene under UHV on a clean platinum (111) surface and over a layer of preadsorbed hydrogen was shown by TPD to proceed by a different mechanism than the steady state high pressure catalytic hydrogenation of ethylene over the same surface. The deuterium distribution obtained during the above two processes were also very different.

An ethylidyne saturated platinum (111) surface was found to adsorb hydrogen with H_2 pressures in excess of 10^{-5} torr between 150 and 320 K; however, ethylene did not chemisorb to this surface and not ethylene nor ethylidyne were hydrogenated during TPD. Evidence for the formation of

an ethylidene intermediate was observed and is further evidence that ethylene decomposition products (ethylidyne and perhaps ethylidene) formed on Pt (111) near room temperature directly participate in the steady state catalytic hydrogenation of ethylene.

Acknowledgements

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Table I:

C_2H_4 / Pt(111)

Kinetic Parameters From TPD

$\beta \sim 30$ K/sec

Process	T_{max} (K)	E_a (Kcal/mole)
C_2H_4 molecular desorption	291	9 ± 2
C_2H_6 formation with desorption	302	18 ± 4
H_2 evolution from $C_2H_4 \rightarrow CCH_3$	320	17 ± 3
C_2H_6 formation when H preadsorbed	252	6 ± 1

Table II:

Model for the Hydrogenation of Chemisorbed Ethylene on Pt (111)

Step	Rate Expression	E_a (kcal/mole)	ν	ref.
1.	$\theta_{C_2H_4}\ \nu\ e^{-E/RT}$	17	4×10^{13}	a
2.	$\theta^2_H\ \nu\ e^{-E/RT}$	9	0.075	b
3.	$K_{eq} = k_3/k_{-3} = \nu\ e^{+E/RT}$	2	0.03	c
4.	$\theta_{C_2H_5}\ \theta_H\ \nu\ e^{-E/RT}$	6	1.47×10^{-3}	c
5.	$\theta_{C_2H_4}\ \nu\ e^{-E/RT}$	9	9.2×10^6	a

a) This work and ref. 2.

b) Ref. 19

c) This work and parameters adjusted to fit the self-hydrogenation process.

Captions for Figures

1. TPD products of ethylene on Pt (111), heating rate: $\beta = 30$ K/sec. Left panel from experiment: $T_{ads}=150$ K, exposure = 6 L (saturation) Right panel from model (see text): $T_{init} = 150$ K, $\theta\,°_{C_2H_4} = 0.3$ a) H_2, 2 amu TPD b) C_2H_6, 30 amu TPD c) C_2H_4, 27 amu TPD

2. Ethane production yield for self-hydrogenation as a function of ethylene exposure over Pt (111). The experimental points fall on the curve generated by the computer model (see text for details).

3. Ethane TPD as a function of hydrogen exposure for H_2 + C_2H_4 on Pt (111). Heating rate: $\beta = 30$ K/sec. Variable hydrogen dose was followed by 0.4 L ethylene dosing. Left panel, experimental C_2H_6 TPD: $T_{ads} = 150$ K. Right panel, computer generated TPD: $T_{init} = 150$ K

4. Deuterium distribution in ethane produced during temperature programmed desorption when a Pt (111) surface was dosed with 30 L deuterium followed by 6 L C_2H_4.

5. Ethane TPD area as a function of hydrogen exposure for H_2 + C_2H_4 on Pt (111). Variable hydrogen dose was followed by 0.4 L C_2H_4. $T_{ads} = 150$ K. The solid line was generated by the model. Inset: Position of the temperature maximum o Experimental Δ Model

6. Ethane TPD area as a function of ethylene exposure. 30 L hydrogen exposure followed by variable ethylene dosing. $T_{ads} = 150$ K. The solid line was generated by the model. Inset: Position of the temperature maximum. o Experimental, Δ Model

7. H_2 TPD following ethylidyne + H_2 exposure on Pt (111). Ethylidyne was deposited by dosing the surface with 10^{-7} torr C_2H_4 at 320 K. H_2 was introduced at 5×10^{-7} torr after crystal cooled to 150 K. a) Ethylidyne saturated surface followed by 30 L H_2 exposure.

b) 1.0 L C_2H_4 followed by 30 L H_2. c) 0.5 L C_2H_4 followed by 30 L H_2.

d) 30 L Hydrogen adsorbed on a clean platinum surface.

8. Hydrogen yield from the prepared surfaces of figure 7. Ethylidyne + H_2 on Pt (111). o The H_2 TPD area as evolved from uncovered Pt (low temperature peak) was normalized to the TPD area of H_2 desorbing from clean Pt (fig. 7d). ● The H_2 TPD area evolved from ethylidyne decomposition (high temperature peak) normalized to the TPD area of H_2 produced from an ethylidyne saturated surface (fig. 7a).

9. H_2 or D_2 TPD from Pt (111) for: a) 6 L C_2H_4 dosed at 320 K (saturated ethylidyne) followed by b) 1200 L H_2, 10^{-5} torr at 150 K c) 1200 L H_2, 10^{-5} torr at 320 K, then cooled immediately to 150 K d) ~ 10^{10} L H_2, 1 atmosphere at 250 K e) ~ 10^{10} L D_2, 1 atmosphere at 250 K, 4 amu TPD.

10. Proposed mechanism for the steady state catalytic hydrogenation of ethylene on Pt(111). The second panel shows schematically the proposed ethylidene intermediates derived from ethylidyne and surface deuterium.

$C_2H_4/Pt(III)$
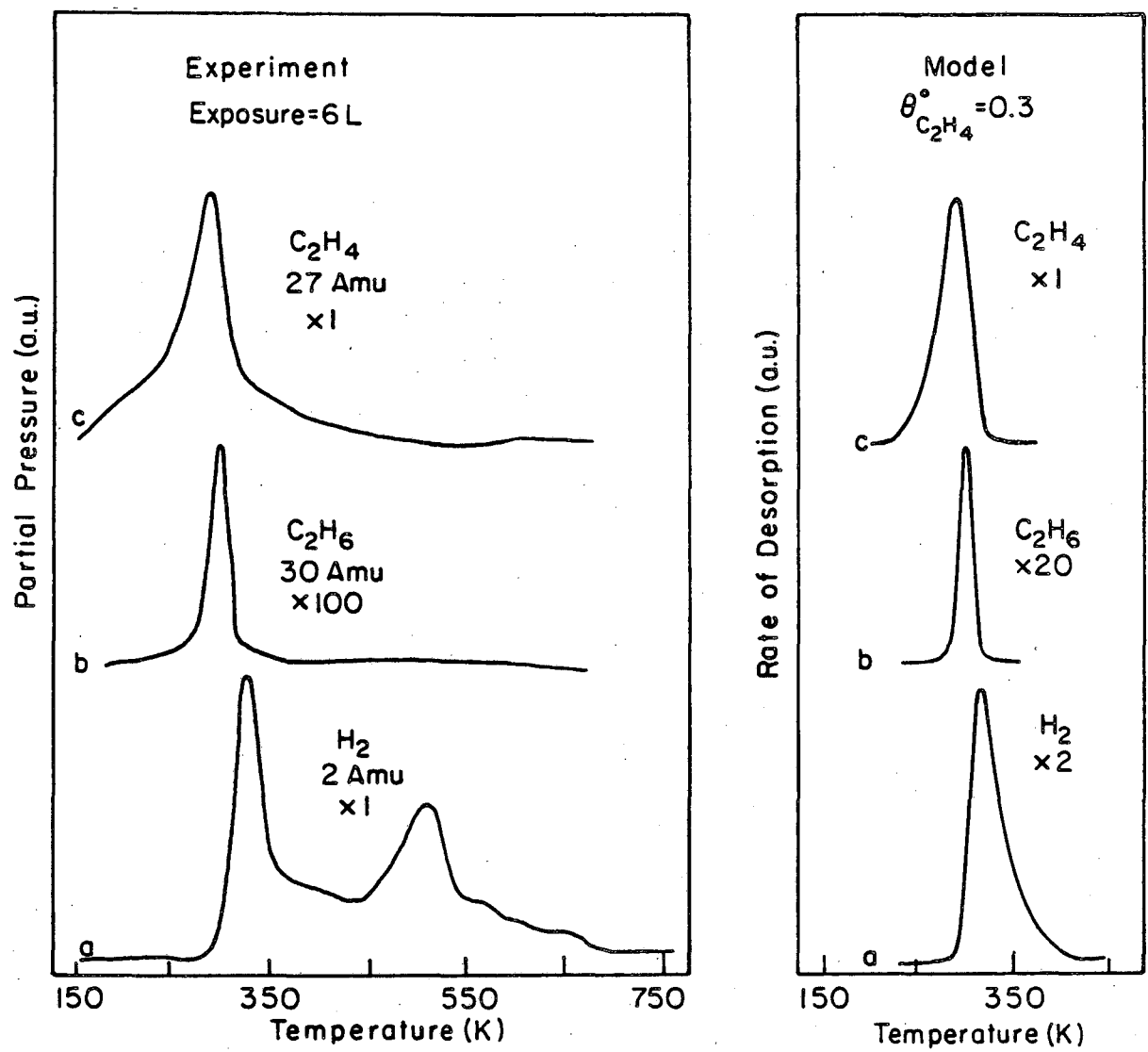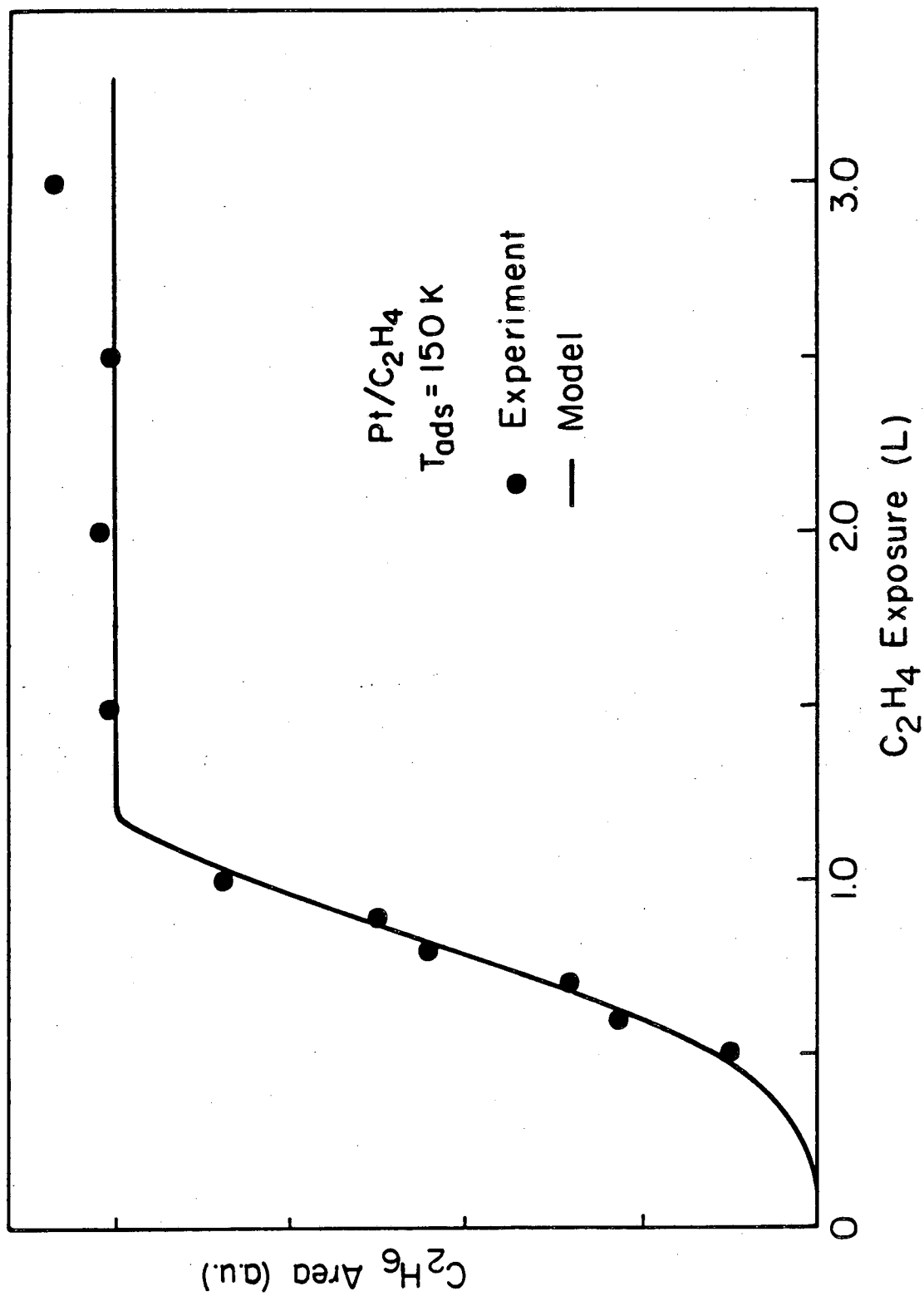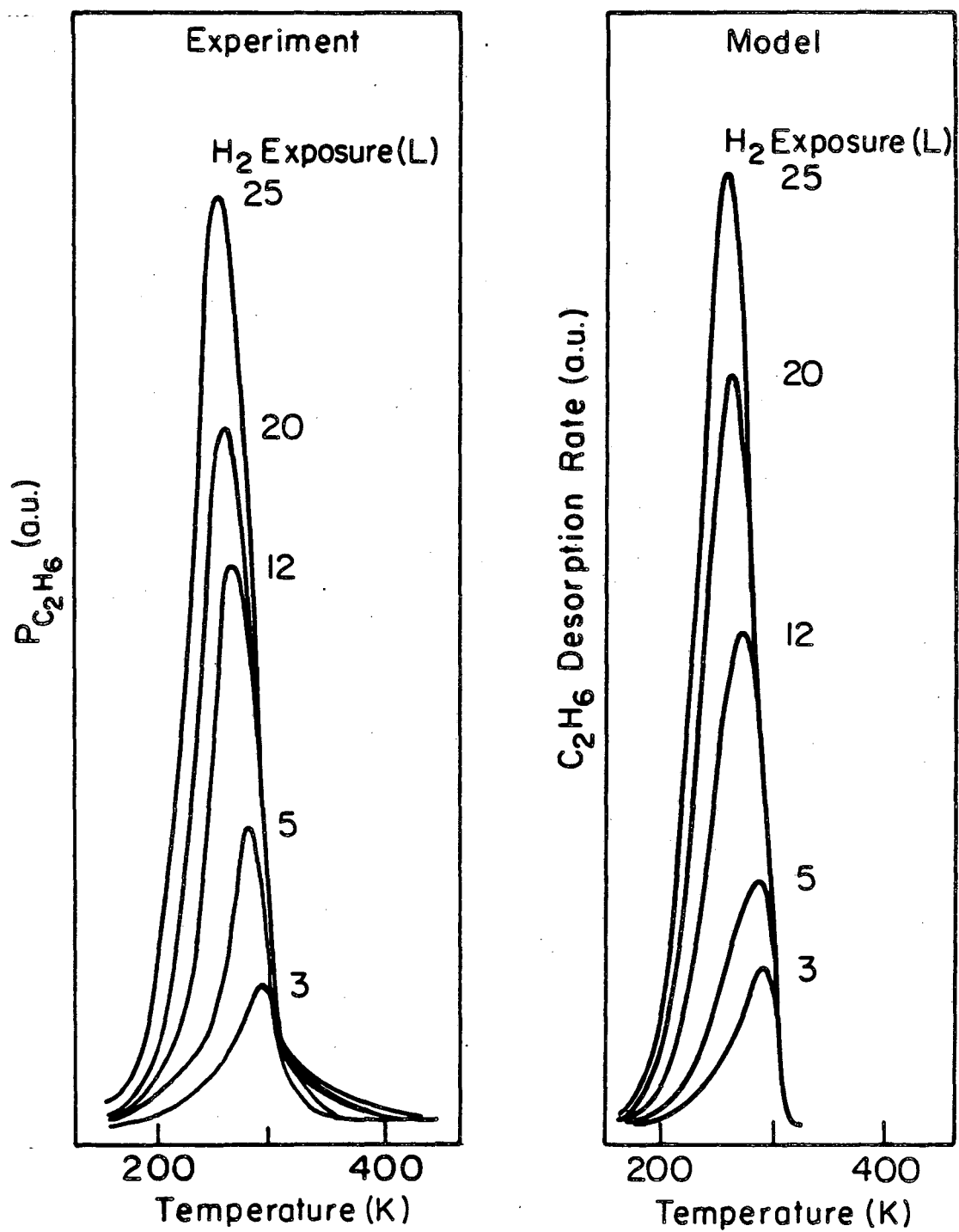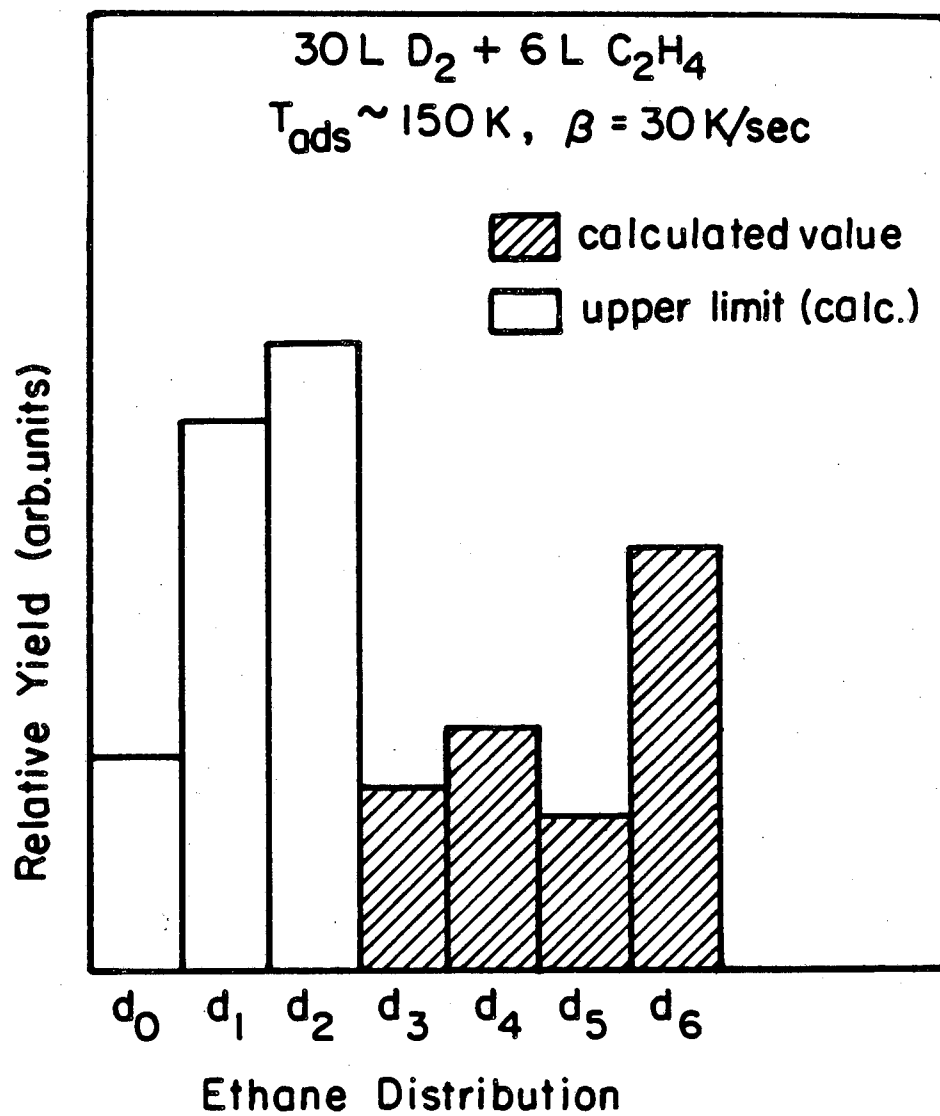
Experiment
Exposure = 6 L

Model
$\theta^{\circ}_{C_2H_4} = 0.3$

C_2H_4
27 Amu
×1

C_2H_4
×1

C_2H_6
30 Amu
×100

C_2H_6
×20

H_2
2 Amu
×1

H_2
×2

Partial Pressure (a.u.)

Rate of Desorption (a.u.)

Temperature (K)

Temperature (K)

XBL 853-5978

Fig. 1

Fig. 2

XBL 853-5976

$H_2 + C_2H_4$ on Pt(III)

Experiment

H_2 Exposure (L)

25

20

12

5

3

$P_{C_2H_6}$ (a.u.)

Temperature (K)

Model

H_2 Exposure (L)

25

20

12

5

3

C_2H_6 Desorption Rate (a.u.)

Temperature (K)

XBL 853-5977

Fig. 3

30 L D_2 + 6 L C_2H_4

$T_{ads} \sim$ 150 K, β = 30 K/sec

calculated value

upper limit (calc.)

Relative Yield (arb.units)

d_0 d_1 d_2 d_3 d_4 d_5 d_6

Ethane Distribution

XBL 855-6281A

Fig.4
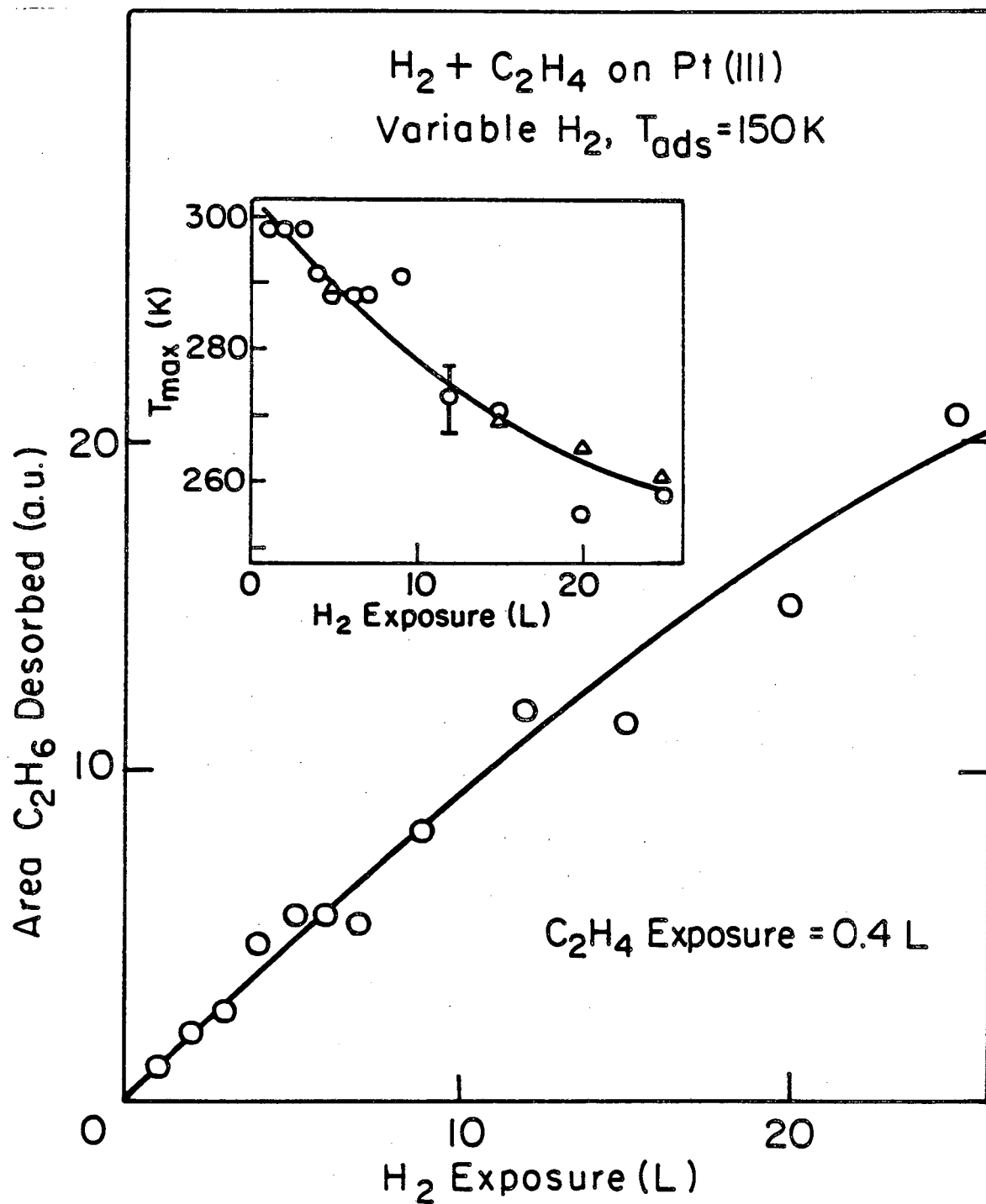
Fig. 5
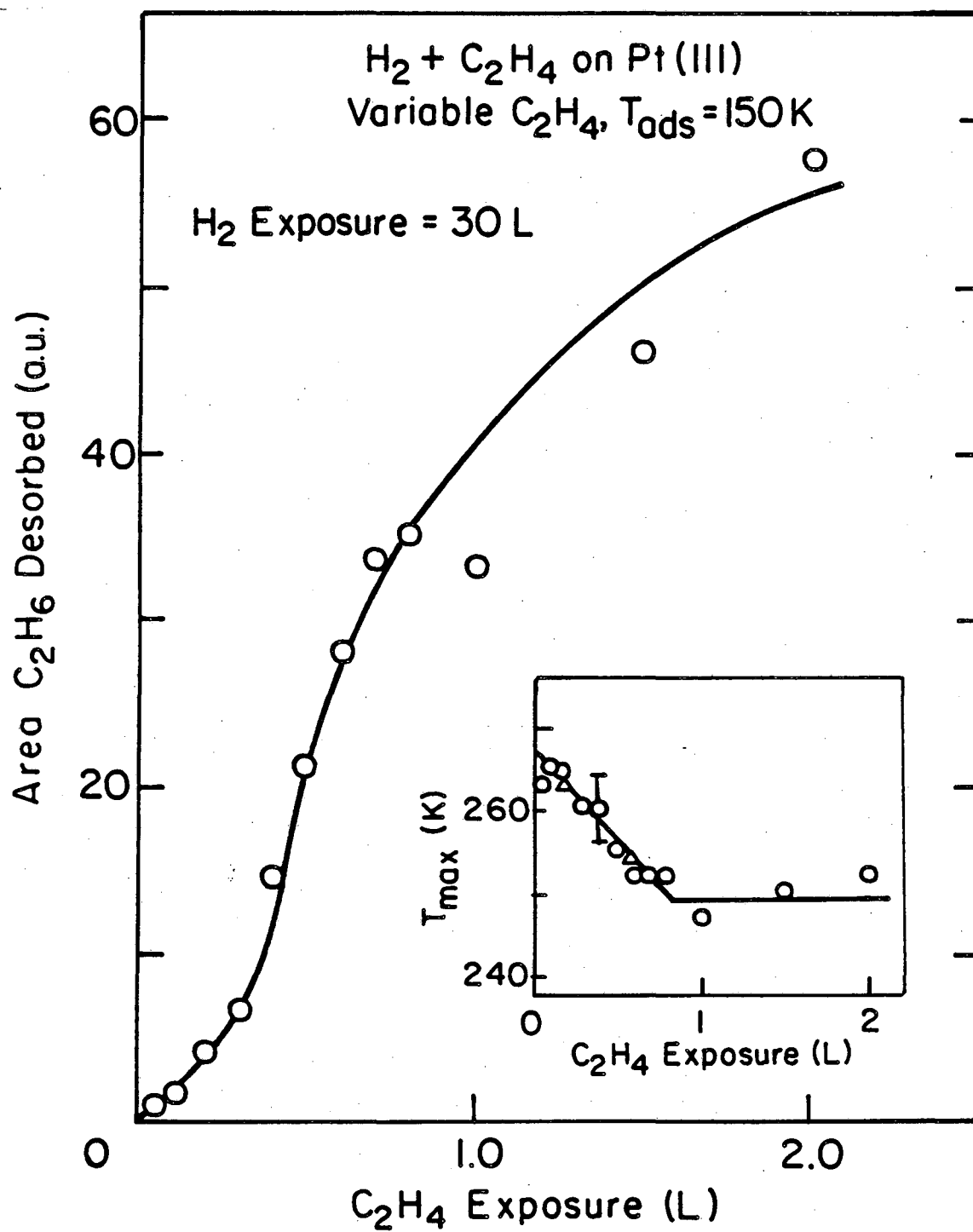
XBL 853-5973

Fig. 6
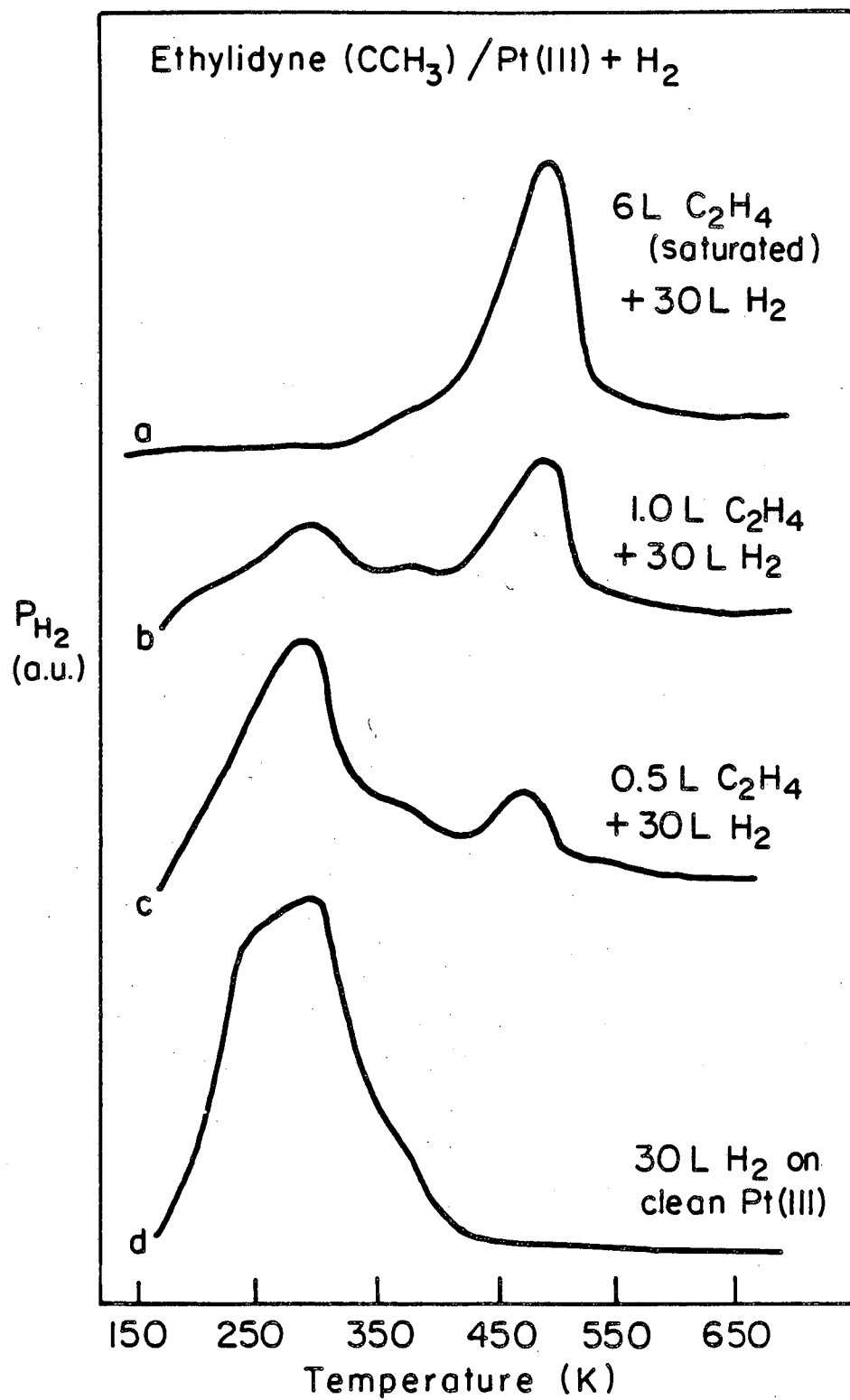
XBL 853-5974

Fig. 7

Fig. 8

XBL 853-5975A

Fig. 9

Fig. 10

31

XBL 846-2494A