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THE CONVERSION OF ACETYLENE TO BENZENE
OVER PALLADIUM SINGLE CRYSTAL SURFACES.
I. THE LOW PRESSURE STOICHIOMETRIC AND
THE HIGH PRESSURE CATALYTIC REACTIONS

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**The Conversion of Acetylene to Benzene
Over Palladium Single Crystal Surfaces
I. The Low Pressure Stoichiometric
and the High Pressure Catalytic Reactions.**

**T. G. Rucker, M. A. Logan¹ , T.M. Gentle²
E. L. Muetterties³ and G. A. Somorjai**

Materials and Molecular Research Division

Lawrence Berkeley Laboratory

and

Department of Chemistry

University of California, Berkeley

Berkeley, California, 94720, USA

1. Present Address: J.C. Schumacher Co., P.O.Box 1158, Oceanside, CA, 92054.
2. Present Address: Dow Corning Corp., Midland, MI, 48640.
3. Deceased January 1984

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Berkeley, California, USA 94720

Abstract

Acetylene cyclotrimerizes to form benzene on palladium single crystals in ultra-high vacuum (UHV) (10^{-12} – 10^{-8} atm) and at atmospheric pressures (10^{-1} –1 atm). The reaction is structure sensitive in both pressure regimes. In UHV the (111) face is the most active followed by the (110) and then the (100) surfaces. At high pressure the (111) and (100) surfaces have equal catalytic activity whereas the (110) face is one-fourth as active. In UHV the reaction products are benzene from cyclotrimerization, ethylene from hydrogenation and hydrogen from decomposition. At high pressures only benzene was detected. The high pressure catalytic reaction proceeds on the bare metal surface. The reaction also proceeds readily on Pd films and Pd supported on alumina.

1.0 INTRODUCTION

The rapid developments in ultra-high vacuum (UHV) surface chemistry and high pressure catalytic studies, both using single crystal surfaces, have led to a growing interest in comparing low pressure and high pressure reactions. Low pressure reactions are mostly stoichiometric with one product molecule formed per metal atom. High pressure reactions have many product molecules formed per metal atom and are thereby catalytic. Correlating the behavior of the same molecules in both stoichiometric and catalytic reaction conditions is important in predicting and modeling high pressure reactions. Only a few reactions proceed readily in both of these conditions. An example of one reaction which occurs in both pressure regimes is the trimerization of acetylene on palladium.

The conversion of acetylene to benzene is a reaction which proceeds readily at pressures ranging from UHV (10^{-12} – 10^{-8} atm) to atmospheric pressures (10^{-1} – 1 atm) on palladium surfaces. This reaction provides a unique opportunity to investigate a synthetic reaction over thirteen orders of magnitude of pressure. We found that the reaction also proceeds on a variety of palladium surfaces: single crystals, evaporated films and small particles supported on alumina.

The cyclization of acetylene to benzene was first reported to occur in small yields by Berthelot [1] in 1866 at elevated temperatures (300 – 400° C) in a glass vial. In the 1940's Reppe [2] discovered that certain homogeneous nickel complexes produced benzene from acetylene in good yield under mild experimental conditions. Since that discovery, other research groups have found numerous homogeneous transition metal systems that catalyze unsubstituted and functionalized acetylenes to form benzene and benzene derivatives [3,4]. For example, cobalt complexes such as $\text{CpCo}(\text{CO})_2$ are used in cyclization steps in the synthesis of natural products such as steroids and Vitamin B₈ [5]. It has also been shown that palladium chloride will easily oligomerize acetylene [6,7].

It has been reported that, in solution, palladium on charcoal will trimerize acetylene in high yields [8]. Also, it has been demonstrated that nickel supported on silica at 300° C is a

suitable catalyst for this reaction [9]. Recently, cyclotrimerization of acetylene has been found on nickel [9] and copper single crystals [10].

Numerous research groups have extensively studied the reactivity and structure of acetylene on palladium and other transition metal surfaces [11-23]. In the original UHV trimerization studies on Pd(111) by Tysoe et al. [17,18] benzene formation was found by temperature programmed desorption (TPD), angle resolved photoemission spectroscopy (ARUPS) and molecular beam measurements. They concluded that the major surface species was a flat-lying acetylenic species at low temperature (<220 K), while at higher temperatures an olefinic species predominated. They also proposed that the low temperature acetylenic species is the precursor in the trimerization reaction, and that the two benzene desorption maxima in the TPD spectra are due to tilted and flat benzene molecules desorbing from the surface. Subsequent work by Sesselman et al. [19] using UPS and metastable deexcitation spectroscopy (MDS) support the low temperature formation of a π /di- σ bonded species and the high temperature formation of a different species (β -state). Here again, the low temperature species is the intermediate in the cyclotrimerization reaction. Electron energy loss spectroscopy (EELS) studies of C_2H_2 adsorption on Pd(111) by Kesmodel et al. [20-22] show formation of C-CH₃ species coadsorbed with CCH fragments. At higher temperatures (>450 K) CCH becomes the dominant species. This group found no evidence for the trimerization reaction. This is in contrast to a recent EELS study by Marchon [23] where vibrational modes due to adsorbed benzene were observed at high C_2H_2 coverages.

This paper reports on the pressure dependence on the cyclotrimerization of acetylene to benzene on palladium surfaces in UHV conditions and at atmospheric pressures. In both pressure regions we assess the influence of surface topography and composition on the metal's catalytic activity [24]. The reaction is structure sensitive in both UHV and atmospheric pressure regimes. In UHV the (111) surface is the most active followed by the (110) and (100) surfaces, while at higher pressure the (111) and (100) are surfaces equal in activity followed by the (110). In both pressure regions the reaction most likely proceeds on the bare metal surface.

2.0 EXPERIMENTAL

The experiments with single crystals of palladium were performed in two separate UHV chambers described in detail elsewhere [25,26]. One chamber was ion pumped and had a base pressure of 1×10^{-10} Torr. It was equipped with a four grid retarding field electron energy analyzer (RFA) for Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED), and a quadrupole mass spectrometer and programmable peak selector for TPD. The crystal was spot-welded to a tantalum foil which masked the edges and was mounted on a high precision manipulator. The crystal was heated by electron bombardment and cooled with a liquid nitrogen reservoir in direct contact with the crystal. In this configuration the crystal could be heated to 1000K, and then cooled to 130K in 2.5 minutes. The crystal temperature was monitored by a chromel/ alumel thermocouple spotwelded to the crystal. Two variable rate leak valves were employed for controlled dosing of the sample surface with the reactant gases.

TPD experiments comprised cleaning the surface with Ar^+ bombardment (5×10^{-5} Torr Ar , 20 mA) and O_2 treatment at 850K (5×10^{-7} Torr) followed by annealing at 950K until the surface was free from contaminants such as carbon, sulfur and silicon as monitored by AES. The crystal was then cooled, flashed to desorb any background gases, rapidly cooled and dosed with the desired amount of reactant gases. While linearly heating at 25K/sec. the desorbing gases were monitored by the mass spectrometer.

The high pressure (HP) experiments on single crystals were performed in a combined high pressure/ UHV chamber which was pumped with a liquid nitrogen trapped oil diffusion pump and had a base pressure of 1×10^{-9} Torr. This chamber, in addition to the standard UHV surface science equipment such as a mass spectrometer, double-pass cylindrical mirror analyzer for AES, LEED optics and Ar^+ sputter gun, was equipped with a high pressure cell which, when raised, enclosed the crystal in a continuous flow batch reactor. The gas mixture in this loop was periodically sampled using a gas chromatograph (GC) with a 3' Poropak N column equipped with a flame ionization detector. The gases were circulated with a magnetically driven micropump. In this chamber, the single crystal was spotwelded to a rotatable manipulator

by tantalum support rods. The crystal was resistively heated and the temperature monitored by a chromel/ alumel thermocouple. The typical sequence for performing the high pressure reaction was as follows: after cleaning the surface as described above, the cell was raised. Acetylene was added to the loop until the desired pressure was reached and then N₂ (an inert carrier gas) was added to bring the total pressure to 20 psi. After the reaction, the loop was evacuated to a pressure of 1×10^{-6} Torr. After lowering the cell, UHV surface science techniques were used to analyze the surface. The initial rate of reaction was calculated from the slope of the product accumulation versus time plot.

Blank experiments (without a Pd crystal) showed no activity, as did the experiments performed on Pd covered by graphitic carbon (obtained by heating the crystal in a hydrocarbon atmosphere at 800K).

The supported catalyst studies were performed in a 2 cm diameter by 5 cm long stainless steel cylinder charged with 5 grams of catalyst. This non-circulating batch reactor has a gas inlet, pressurizing hydraulic piston, and an evacuating mechanical pump at one end, and a two column gas chromatograph equipped with a flame ionization detector at the other. The temperature was controlled by a ceramic block heater, and monitored with a chromel/alumel thermocouple. The temperature was allowed to stabilize for 30 minutes prior to adding the acetylene. The Pd/Al₂O₃ was cleaned by flowing O₂ (420K, 1hr), followed by hydrogen (450K, 1 hr) over the catalyst, and then heating in vacuo (480K, 1 hr). After adding the purified acetylene, the reaction mixture was periodically sampled and analyzed with the GC. The fourth system used in this series of experiments on the cyclotrimerization of acetylene was a film reactor. This system consisted of a glass bell jar with an area of 36 cm², and a volume of 1.2 l mounted on a liquid nitrogen-trapped oil diffusion pump. The system also had an ionization gauge and a TC gauge to monitor the pressure in the operating regions. A visible layer of palladium was deposited onto the walls of the bell jar by resistively heating a piece of Pd foil (99.9% pure). After adding the purified acetylene to 250 millitorr, the reaction mixture was periodically sampled by a GC. All the reactions were performed at room temperature. After each reaction the bell jar was again coated with twice the original amount of Pd (as

measured by time) to cover the carbonaceous deposit from the previous reaction. After two reactions, the bell jar was cleaned in aqua regia, followed by an ethanol rinse and drying. Blank experiments showed no activity of the uncoated surface.

Acetylene (Matheson) was passed through a 195K acetone/dry ice bath prior to use in order to remove the acetone stabilizer and then vacuum distilled into a glass bulb. Benzene was dried over calcium hydride. Spectroscopic grade ethylene was used without further purification. The palladium single crystals were spark erosion cut from single crystal rods (Metals Research Ltd.) to within $\pm 1^\circ$ of the desired orientation, and prepared by standard metallographic techniques, which produced optically flat and ordered surfaces. Palladium supported on alumina (5%) was obtained from Aldrich (Lot #CK0220 KE).

3.0 RESULTS

We have investigated the conversion of acetylene to benzene over a twelve orders of magnitude pressure range (1×10^{-12} atm - 1 atm) using palladium catalysts (single crystals, films and alumina supported). The experiments are divided into two classes:

- 1) At low pressures (1×10^{-12} - 1×10^{-8} atm) the reaction is stoichiometric and the formation of benzene is monitored by temperature programmed desorption of molecular benzene after dosing with acetylene at 130 K.
- 2) At high pressures (1×10^{-1} - 1 atm) the reaction is catalytic and benzene formation is monitored by gas chromatography.

3.1 Low pressure, stoichiometric reaction studies over palladium single crystal surfaces.

Following the adsorption of acetylene on the Pd single crystals acetylene, ethylene, benzene and hydrogen were detected as desorption products. In order to gain a better understanding of the reaction ethylene, benzene and hydrogen were adsorbed separately on the clean Pd crystals. Table 1 lists the adsorbate molecules, the desorption products and temperatures, relative amounts and the activation energies of desorption for the (111), (100) and (110)

palladium single crystal surfaces.

3.1.1 Pd (111)

On the Pd(111) face, dosing 6 Langmuirs (L) of acetylene produced benzene with two distinct desorption peaks at 250 K and 490 K. The low temperature peak was 2.5 times larger than the high temperature peak (Fig. 1). Acetylene, ethylene and hydrogen were also detected as desorption products. Acetylene and ethylene desorbed at 190 K and 310 K respectively. Hydrogen, the only other product detected, had a broad desorption peak from 430 K to 830 K, with a maximum at 450 K (Table 1). At low acetylene coverages (0.5 L) the temperatures of the benzene desorption maxima remained unchanged. The amount of benzene formed decreased, with the area under the high temperature peak decreasing more rapidly than the area under the low temperature peak. No C_4 products were detected.

To determine whether the products formed before or during desorption C_6H_6 , C_2H_4 , H_2 were adsorbed separately on clean Pd(111) at 130 K and TPD spectra of each were taken as a function of coverage. Benzene undergoes reversible and irreversible chemisorption, with the fraction of reversibly bound benzene increasing with exposure. At low coverages (1.0 L) there was primarily decomposition as characterized by a broad hydrogen trace extending from 520 K to 720 K with a maximum at 545 K. Benzene had two weak desorption peaks at 260 K and 520 K. With exposures greater than 2 L the hydrogen spectrum remained unchanged and the benzene maxima occurred at 235 K and 510 K with a 1:10 intensity ratio. Acetylene and ethylene were not observed as desorption products. Dosing hydrogen on the clean surface yielded a single desorption peak of H_2 at 310 K. The peak does not shift with increasing hydrogen exposure. With ethylene (1.0 L), reversible desorption occurred at 300K with hydrogen desorbing at 370 K and 430 K in a 1:1 ratio. Higher coverages of ethylene (>2 L) increased molecular desorption of ethylene only. No benzene desorption was detected following ethylene exposure.

3.1.2 Pd(100)

On the Pd(100) surface, following an exposure of 6 L of acetylene a broad, continuous benzene

desorption peak was observed from 250 K to 490 K with three maxima at 260 K, 380 K and 470 K (Fig. 2). At exposures below 3 L no benzene was detected. This surface formed one-twentieth as much benzene as the (111) crystal face. With a 6 L dose of acetylene, in addition to cyclotrimerization, reversible desorption, hydrogenation and decomposition were also observed. Acetylene desorbed at 180 K with a shoulder at 250 K, and ethylene desorbed in a single peak at 305 K. The hydrogen desorption from the decomposition reached a maximum at 420 K, followed by a broad plateau from 495 K to 625 K. At low coverages of acetylene (1.0 L) there was primarily decomposition. No C_4 fragments were detected. Benzene dosed on the crystal at low coverages (1.0 L) yielded a weak maximum at 310 K, with a tail extending to 535 K. At an exposure of 6.0 L, three poorly resolved benzene maxima at 220 K, 375 K and 525 K were observed, along with a hydrogen peak at 575 K which had a high temperature shoulder at 665 K. When hydrogen alone was dosed on the surface, at all coverages it desorbed at 310 K in one peak. Ethylene (0.5 L) gave molecular desorption at 260 K and 310 K in a 1:5 ratio with hydrogen desorbing at 365 K. Larger ethylene doses increased the low temperature reversible desorption peak without affecting the hydrogen desorption. No benzene was detected from ethylene.

3.1.3 Pd(110)

The Pd(110) surface produced one sixth the amount of benzene than the (111) face and three times more benzene than the (100) face. On the (110) face, benzene desorbed at 250 K and 420 K in a 1:3 ratio after a 6 L dose of acetylene (Fig. 3). With acetylene coverages below 3 L, no benzene was detected. Molecular desorption of acetylene occurred at 180 K with a broad shoulder plateau extending to 500 K. Ethylene desorbed at 260 K, and hydrogen in a broad peak centered at 490 K. When the surface was dosed with 6 L of benzene, molecular desorption occurred at 250 K, with a shoulder extending to 425 K. At low coverages (1.0 L) a single peak at 260 K was observed. The hydrogen from decomposed benzene had maxima at 475 K and 535 K which increased in area with increasing amounts of benzene up to 3 L, after which they remained constant. Hydrogen desorbed at 310 K at low coverages when adsorbed on the clean surface, and the desorption temperature decreased with increasing coverage.

3.1.4 Summary of low pressure cyclotrimerization studies.

Benzene forms from adsorbed acetylene on all three low Miller index planes of palladium. The cyclotrimerization of acetylene was most facile on clean Pd(111) followed by the (110) face which was 18% that of the (111) surface and then the (100) surface, which formed 5% as much as the (111) face (Fig. 4). On the (111) surface, benzene formed at exposures above 0.5 L. On the other surfaces, only after exposures greater than 3 L of acetylene did benzene become observable. Ethylene and hydrogen desorption were detected on all surfaces at all coverages and no C₄ products were seen.

3.2 High pressure catalytic reaction studies on palladium single crystal surfaces.

We have extensively studied the cyclotrimerization of acetylene on three low Miller index planes of palladium ((111), (110) & (100)) at high pressures (200 Torr to 1200 Torr) in the temperature range of 273-573 K. For all the temperature and pressure conditions used in this study, benzene was the only product detected. Due to the large acetylene peak in the GC trace, ethylene could not be detected below five mole percent relative to acetylene. As was observed in UHV conditions, the reaction showed structure sensitivity for the formation of benzene (Fig. 4). It was found that the (111) and the (100) surfaces were approximately equal in catalytic activity and the (110) surface was one-fourth as active. The (111) and (100) surfaces had a turnover frequency (T.F.) of 0.048 molecules site⁻¹ sec⁻¹ and the (110) face had a T.F. of 0.014 molecules site⁻¹ sec⁻¹ (200 Torr acetylene, 850 Torr N₂ or Ar at 575 K). The turnover frequency is defined as the number of molecules formed per metal atom per second assuming 1.5×10^{15} metal atoms per cm² on the single crystal surface. Turnover frequency was constant for over ten hours of reaction time, and the rates shown in Fig. 4-6 are obtained within the first three hours. No correction was made for the different number of surface atoms on the various faces. On the more active surfaces the reaction had up to fifty percent conversion of acetylene to benzene or roughly a 20 mole percent yield of benzene. At these conversion percentages, the reaction was limited by either surface poisoning or by product concentration. The slope of the turnover frequency plotted versus 1/T, assuming Arrhenius kinetics, yields the apparent activation energy of the reaction, calculated as 2 kcal

mol^{-1} on all three surfaces (Fig. 5). Plotting the reaction rate as a function of acetylene pressure showed that the reaction was first order in acetylene, with the rate law (Fig. 6):

$$\text{Rate} = kP_{\text{C}_2\text{H}_2}^{+1}$$

Analysis by AES and CO titration after the reaction, found a partially carbon covered surface. After heating the crystal to 650 K and exposing to 1×10^{-6} Torr of hydrogen, the surface remained carbon-covered, implying a stable graphitic overlayer. CO titration determines the percentage of bare metal sites since CO does not adsorb on carbon overlayers at low pressure. After the trimerization reaction (200 Torr acetylene, 850 Torr N_2 , 300 K, 3 hours reaction time), it was estimated that only 5-7% of the Pd(111) surface was composed of bare metal sites, while the same conditions yielded 12-15% bare sites on Pd(100) and less than 2% on the (110) face, the least active surface.

From TPD studies it was determined that CO binds more strongly to the partially carbon covered metal than C_2H_2 does. In order to determine if the reaction proceeded on the bare metal or a carbonaceous overlayer, we added 0.2 Torr of CO into the circulating gases of a reaction at room temperature, three hours after the start of the reaction. The reaction was immediately quenched and the rate of benzene formation was zero. Subsequent heating of the crystal to 485 K, which is above the desorption temperature of CO, restored the reaction rate to within 15% of its original value. At lower reaction temperatures the poisoning rate of the reaction decreased as determined by higher reaction rates and less carbon buildup.

At the beginning of the cyclotrimerization reaction a small amount (10^{-4} times the amount of benzene) of C_4 products were detected. This peak disappeared one hour into the reaction. Using ethylene as the reactant gas, instead of acetylene, produced only very small quantities of benzene (two percent the amount as from C_2H_2) and ethane showed no activity for the formation of benzene. A mixture of methyl acetylene and acetylene produced only benzene.

3.3 High pressure reaction studies on palladium films and alumina supported palladium particles.

We have also extended this study to palladium surfaces other than single crystals. The other two surfaces investigated in this study are palladium films coated on glass and palladium supported on alumina. Both of these surfaces catalyze benzene formation.

In the Pd film reactor, the chamber was filled to 0.25 Torr of acetylene and the reaction mixture periodically sampled. Benzene, ethylene and ethane were the only observed products, and all formed within fifteen minutes. The reaction continued until all of the acetylene was consumed (approx. 100 minutes). Roughly equal mole percentages benzene and ethylene formed with less ethane being produced (Fig. 7). Under these isothermal conditions the turnover frequency was about 0.01 molecules site⁻¹ sec⁻¹ assuming a Pd film area of 36 cm² and a Pd atom concentration of 1×10^{15} atoms cm⁻² (actual number of active metal sites not determined due to unknown surface morphology)

Analysis of surface carbon coverage after the reaction was not possible.

Palladium supported on alumina also formed benzene. In contrast to the Pd film, this reactor had to be heated to 430 K to see appreciable amounts of benzene. At room temperature small amounts of benzene formed (Fig. 8). As in the film reactor, significant amounts of ethylene formed, with a higher percentage of benzene forming at elevated temperatures. At 430 K acetylene was found to completely react to form C₆H₆, C₂H₄ and C₂H₆.

4.0 DISCUSSION

The most interesting feature of the acetylene-palladium chemistry is the low pressure stoichiometric, and high pressure catalytic, formation of benzene on a variety of surfaces (single crystals, films and supported on alumina). The trimerization under UHV conditions has been studied by our group and others (11,24,17-20). These studies have detected benzene formation with ultraviolet photoelectron spectroscopy, TPD metastable deexcitation spectroscopy, EELS and other techniques (11,17,19,23). One exception is the EELS study by Kesmodel et al. (20). They only observed the formation of surface CH, CCH and \equiv C-CH₃ fragments and no benzene. Subsequent EELS work by Marchon (23) found evidence for benzene at higher acetylene coverages. Ours is the first systematic study of this unique reaction at both high

pressures and in UHV. In UHV there is structure sensitivity for the reaction, with the (111) face the most active followed by the (110) with one-sixth the activity and the (100) with one-twentieth the activity of the (111) surface (Fig. 4). At low pressures, the activity was determined by comparing the area under the thermal desorption traces, and at high pressures, the activity was determined by comparing the turnover frequency.

In UHV, benzene desorbs with two maxima at 250 K and 450 K, on the (111) face when formed from acetylene. When the surface was dosed with benzene there were desorption maxima at the same temperatures, suggesting that benzene formation is desorption rate limited rather than reaction rate limited. Thus, acetylene forms benzene upon adsorption and it exists in that form on the metal surface. Similar thermal desorption traces of H₂ from the C₂H₂ and C₆H₆ doses further substantiate this proposition. In both cases hydrogen desorbs in a broad high temperature peak centered around 450-540 K. These similarities between benzene desorption traces exist on the other surfaces (Table 1). The low and high temperature maxima in the benzene desorption show that benzene forms readily and also that some benzene formed decomposes on the metal surface. The TPD spectra obtained for hydrogen, ethylene and benzene correlate well with previous studies [27-30].

Using Redhead's [31] method of calculating activation energies of desorption for the UHV reactions from desorption maximum, the activation energies for benzene formation are 15 and 30 kcal mol⁻¹ for the low (260 K) and high (520 K) temperature peaks on the (111) surface (Pre-exponential is 1×10^{13}). Contrasting these values with those from the high pressure data shows large differences in activation energy. At high pressure, the cyclotrimerization reaction has an activation energy of 2 kcal mol⁻¹ (Fig. 5). For a high pressure reaction this is an extremely low value. For comparison, the formation of methane from CO and H₂, a facile reaction on iron, has an E_a of 24 kcal mol⁻¹ and H₂/D₂ exchange on Pt has a 4 kcal mol⁻¹ activation energy [32,33]. This low activation energy could suggest formation of benzene on an overlayer of ethylidyne or other carbonaceous fragments onto which it would be loosely bound. From CO titrations it can be seen that the reaction rate is dependent on the number of metal sites available. As mentioned previously, on the (111) and the (100) surfaces approximately

5-7% and 12-15% of the surface was bare after three hours of reaction time and on the less active (110) surface only 1-4% of the surface was bare. The differences in bare metal sites on the (111) and (100) surfaces which have similar turnover frequencies are most likely due to different poisoning rates. Also, when CO was added to the room temperature reaction one hour after the start, the rate decreased to almost zero. Subsequent heating to 485 K, which is above the desorption temperature of CO, restored the rate to within 15% of its original value. CO binds only to the metal surface and since it binds more strongly than acetylene, it would displace acetylene. The CO titrations, CO poisoning experiments and the structure sensitivity show that the bare metal atom is the active site for the high pressure reaction.

The low activation energy for this reaction can also be explained by incorporating an adsorption equilibrium constant into the rate law [34]. The apparent activation energy, which is determined from the slope of the $\ln k$ versus $1/T$ plot, equals the combination of the surface process activation energy and the heat of chemisorption. We were unable to extend the experimental parameters to regions of high acetylene surface coverage to test this hypothesis.

The (110) surface, the least active face, is the most open surface and leads to the highest decomposition rate of both acetylene and benzene as seen by the low percentage of bare Pd atoms. Therefore, the amount of irreversibly bound carbon in the catalytic steady state reaction limits the rate by blocking sites.

If the percentage of open, or active sites is taken into account, the reaction still exhibits structure sensitivity (Table 2). The (111) surface is still the most active, followed by the (110) and then the (100) face. This is the same order of activity as seen in UHV. The relative values of the activity differ, however this may be due to the inaccuracy in determining the percentage of open sites with CO titrations.

Product distributions at low and high pressures differ. In UHV, in addition to benzene formation, approximately 20% as much ethylene forms. At high pressure on single crystals less than 5% ethylene forms. Hydrogen could not be detected at high pressure. The presence of hydrogen would lead to rapid hydrogenation to ethylene and ethane. Also a rougher surface

which has more decomposition would allow self hydrogenation. In UHV no C₄ fragments were detected whereas at atmospheric pressures small amounts (<.1% of the benzene formed) of C₄ fragments were observed during the first hour of the reaction, but were subsequently reduced in concentration during the reaction.

Benzene formation was detected on Al₂O₃ supported palladium and on palladium films on glass. Quantitative data was difficult to obtain. Nevertheless, these experiments show that the cyclotrimerization proceeds readily on a variety of palladium surfaces.

The most difficult question to address is that of possible mechanisms for the reaction. It is likely that several mechanisms exist and there may be a gradual transition from one to another as a function of pressure. One possible reaction path involves a metalla cyclopentadiene as an intermediate. In organometallic chemistry numerous studies have investigated possible routes for [2+2+2] cycloadditions [5]. Spectroscopic evidence (NMR, IR) suggest that two acetylenes sequentially displace two ligands to form a metallacyclopentadiene intermediate. This is followed by the insertion of another acetylene to form either a metallacycloheptatriene and then benzene, or to form benzene through a Diels-Alder type addition [35]. The first portion of this mechanism is well understood, but the addition of the final acetylene is very rapid and the pathway has not been determined. Another reaction scheme involves the concerted trimerization of three acetylene molecules [36]. One could also suggest the formation of a cyclobutadiene intermediate on the surface [37,38]. Since no C₄ products were detected at low pressure and only small amounts at high pressure this mechanism seems improbable; and has been ruled out in the homogeneously catalyzed reaction [37]. Analysis of product distribution and yields does not provide enough information to propose a mechanism but allows us only to rule out various possibilities.

5.0 CONCLUSIONS

From this surface science study of acetylene chemistry on palladium surfaces numerous important results were obtained which are outlined below.

1. The cyclotrimerization of acetylene proceeds readily in ultra-high vacuum and at atmo-

spheric pressures.

2. The reaction is structure sensitive in both pressure regions.

a) In UHV the activity ratio of the (111):(110):(100) faces is 100:18:5 respectively.

b) At atmospheric pressures the (111) and the (100) surfaces have equal activity followed by the (110) surface which is one-fourth as active. If the percentage of open or active sites is taken into account the reaction exhibits the same structure sensitivity ordering as in UHV [(111)>(110)>(100)].

3. At atmospheric pressures the reaction proceeds on the bare metal surface, with an activation energy of 2 kcal/mol and with a first order pressure dependence in acetylene.

4. On single crystals in UHV acetylene produced benzene, ethylene by hydrogenation and hydrogen from decomposition. At high pressures on single crystals only benzene was detected.

5. Acetylene also cyclotrimerizes on Pd film and on small Pd particles supported on alumina.

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FIGURE CAPTIONS

Figure 1. Presented in this figure are the thermal desorption spectra for 6 L of acetylene dosed at 130K on Pd(111). The heating rate was 25K/sec. Benzene from cyclotrimerization, ethylene from hydrogenation and hydrogen from decomposition were detected.

Figure 2. The desorption products for 6 L acetylene dosed on the Pd(100) surface are presented. The heating rate was 25K/sec. Benzene, ethylene, hydrogen and acetylene were the only molecules desorbing from the surface.

Figure 3. This figure presents the products and desorption temperatures from the stoichiometric reaction of 6 L of acetylene dosed on the Pd(110) surface at 130K. The heating rate was 25K/sec. Benzene has two desorption maxima at 265K and at 425K. Ethylene desorbs at 265K and reversible molecular desorption of acetylene occurs at 175K. Hydrogen has a single maxima at 495K. No other products were detected.

Figure 4. The relative amount of benzene formed on single crystals in UHV and at atmospheric pressures is shown here. In UHV the (111) face is the most active followed by the (110) and then the (100). At higher pressures (1 atm.) the (111) and the (100) faces show equal activity and the (100) is $\frac{1}{4}$ as active.

Figure 5. The activation energy for the catalytic reaction of 2 kcal mol⁻¹ is determined by calculating the slope of the log Turnover Frequency plotted versus 1/T. This value is obtained on all three low Miller index planes of palladium.

Figure 6. Plotting the turnover frequency as a function of acetylene pressure shows that the cyclotrimerization reaction is first order in acetylene on all three surfaces. The (111) face is more active than the (110) face.

Figure 7. On palladium films coated on glass, benzene forms from acetylene at room temperature with 250 mTorr of acetylene (~ 10 – 20 ML). Other products detected were ethylene and ethane which are formed with hydrogen from decomposed acetylene. Relative product distribution is measured by GC counts and corrected for GC sensitivity.

Figure 8. This figure shows the relative product distribution of acetylene over palladium supported on alumina at 2 atm. At temperatures below 470K there is limited conversion of acetylene to benzene and ethylene. At temperatures above 470K the relative amount of benzene increases.

Table 1. Desorption Products from acetylene, ethylene and benzene over Pd(111), Pd(100) and Pd(110) single crystals in UHV. Relative areas are determined by integrating peak area and normalizing to acetylene. Corrected for mass spectrometer sensitivity.

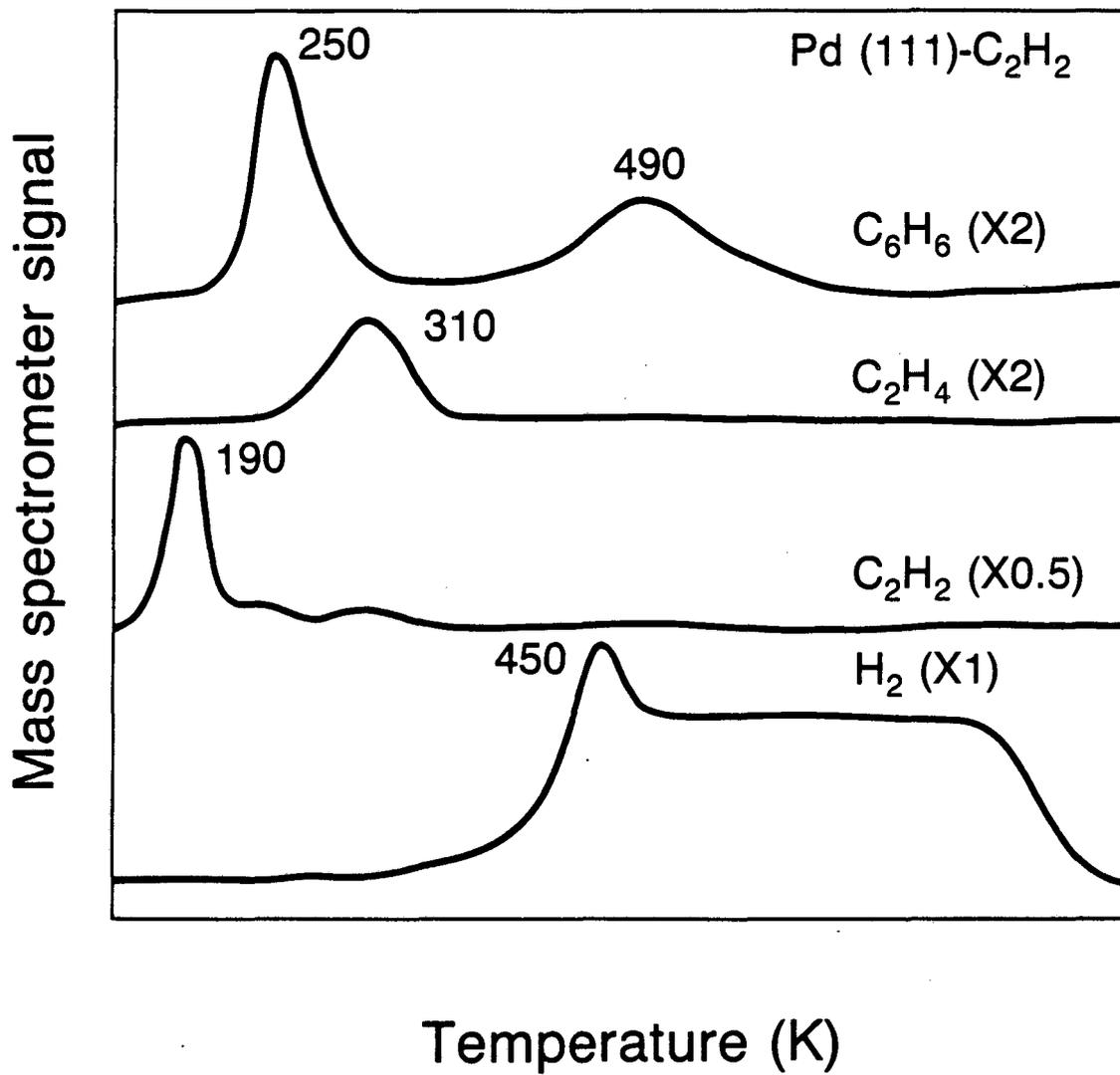
Crystal Face	Dose Molecule	Desorption Product	Desorption Temperature (K)	E_a (kcal/mol)	Relative Areas (for C ₂ H ₂ adsorp.)
(111)	C ₂ H ₂	H ₂	450 (430-830)	26.3	2.0
		C ₂ H ₂	190	10.8	1.0
		C ₂ H ₄	350	20.3	0.4
		C ₆ H ₆	250,490	14.3, 28.7	1.7
	C ₂ H ₄	C ₂ H ₄	300	17.3	
	C ₆ H ₆	H ₂ C ₆ H ₆	545 (520-720) 260, 520	32.0 14.9, 30.5	
(100)	C ₂ H ₂	H ₂	420 (495-625sh)	24.5	1.3
		C ₂ H ₂	180 (250sh)	10.2	1.0
		C ₂ H ₄	305	17.6	.2
		C ₆ H ₆	260,380,470	14.9,22.1,27.5	.1
	C ₂ H ₄	C ₂ H ₄	260,310	14.9,17.9	
	C ₆ H ₆	H ₂ C ₆ H ₆	575 (655sh) 220,375,525	33.8 (39.3) 12.5,21.8,30.8	
(110)	C ₂ H ₂	H ₂	490	28.7	0.7
		C ₂ H ₂	180 (to 500sh)	10.2 (29.3sh)	1.0
		C ₂ H ₄	260	14.9	0.2
		C ₆ H ₆	250,420	14.3,24.5	0.1
	C ₂ H ₄	C ₂ H ₄	260	14.9	
	C ₆ H ₆	H ₂ C ₆ H ₆	475,535 250 (to 425sh)	27.8,31.4 14.3 (to 24.8)	

Table 2. Relative catalytic rates, according to open active sites. Percentage of open sites determined by CO titrations after three hours of reaction time.

Crystal Face	Turnover Frequency*	Percentage of Open Sites	Catalytic Rates**
(111)	0.048	7	0.96-0.68
(100)	0.048	12-15	0.40-0.32
(110)	0.014	2	0.7

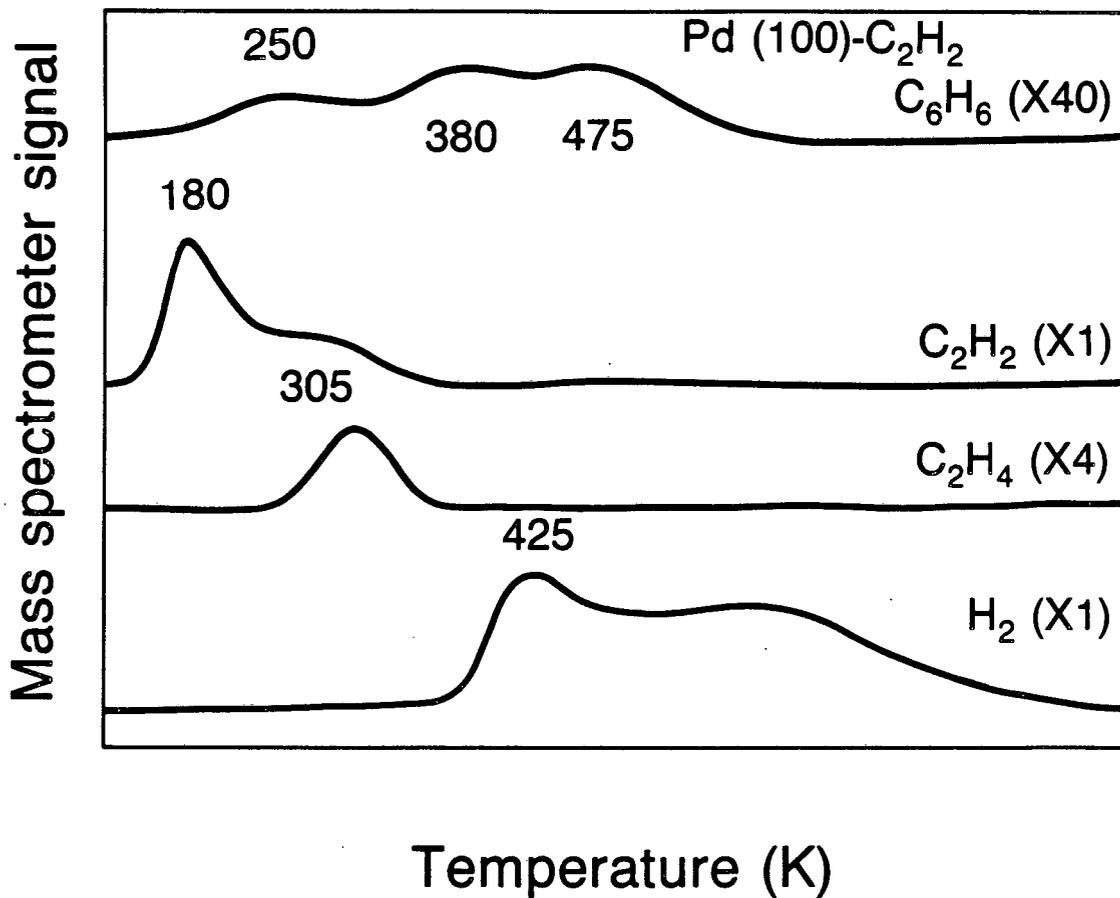
* units of molecules/site•sec

** units of molecules/open site•sec



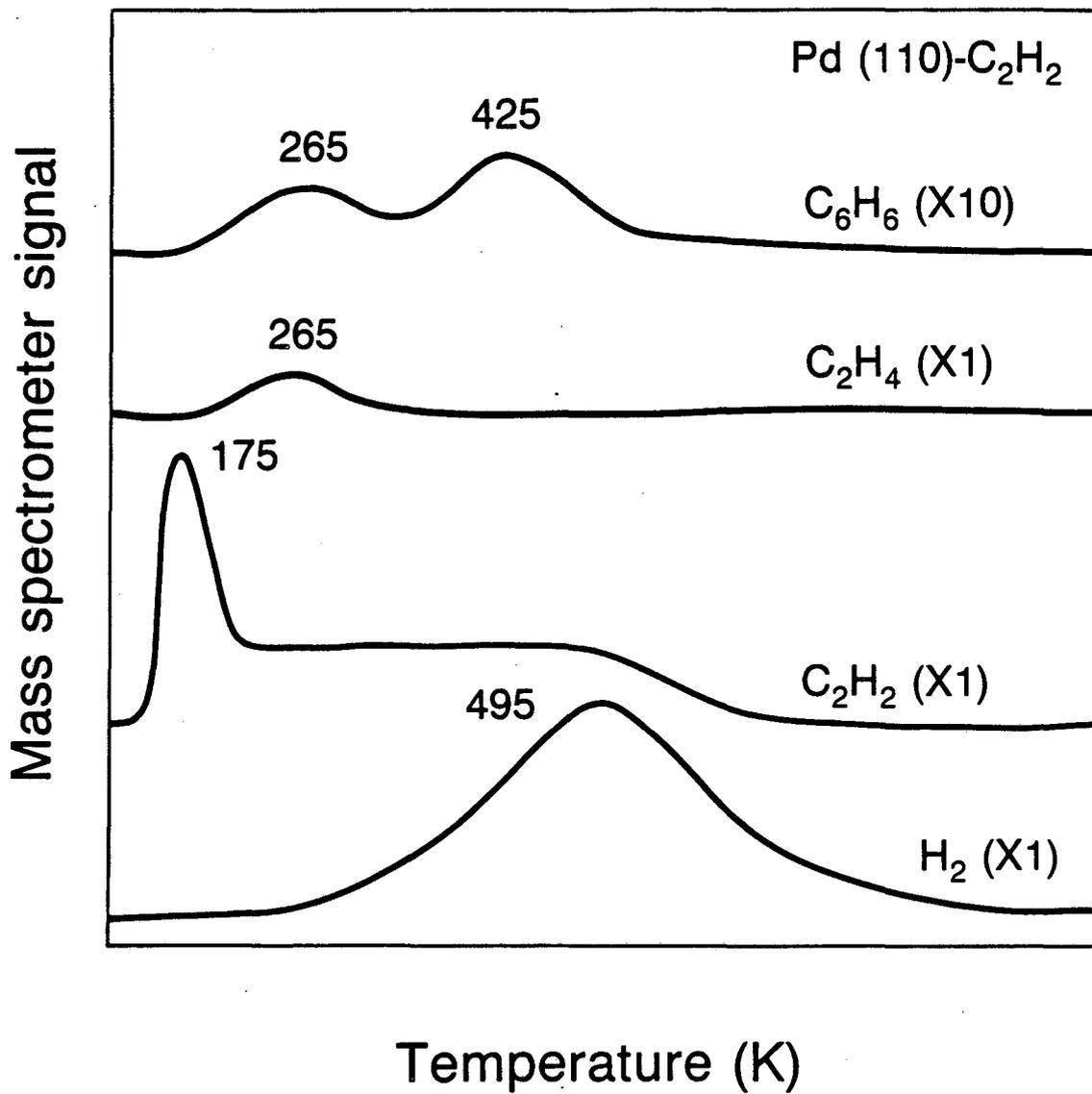
XBL 856-11208

FIGURE 1



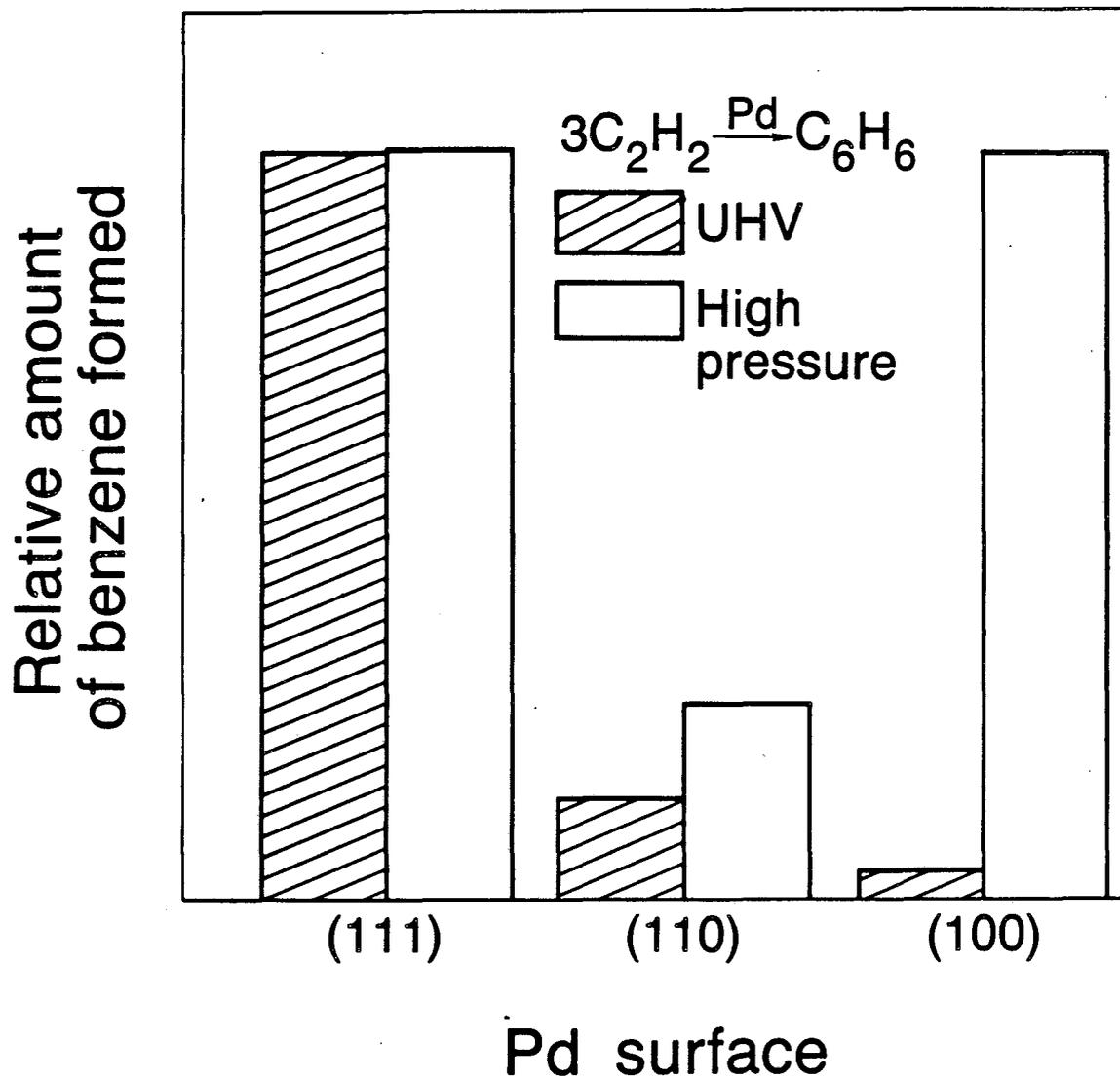
XBL 856-11202

FIGURE 2



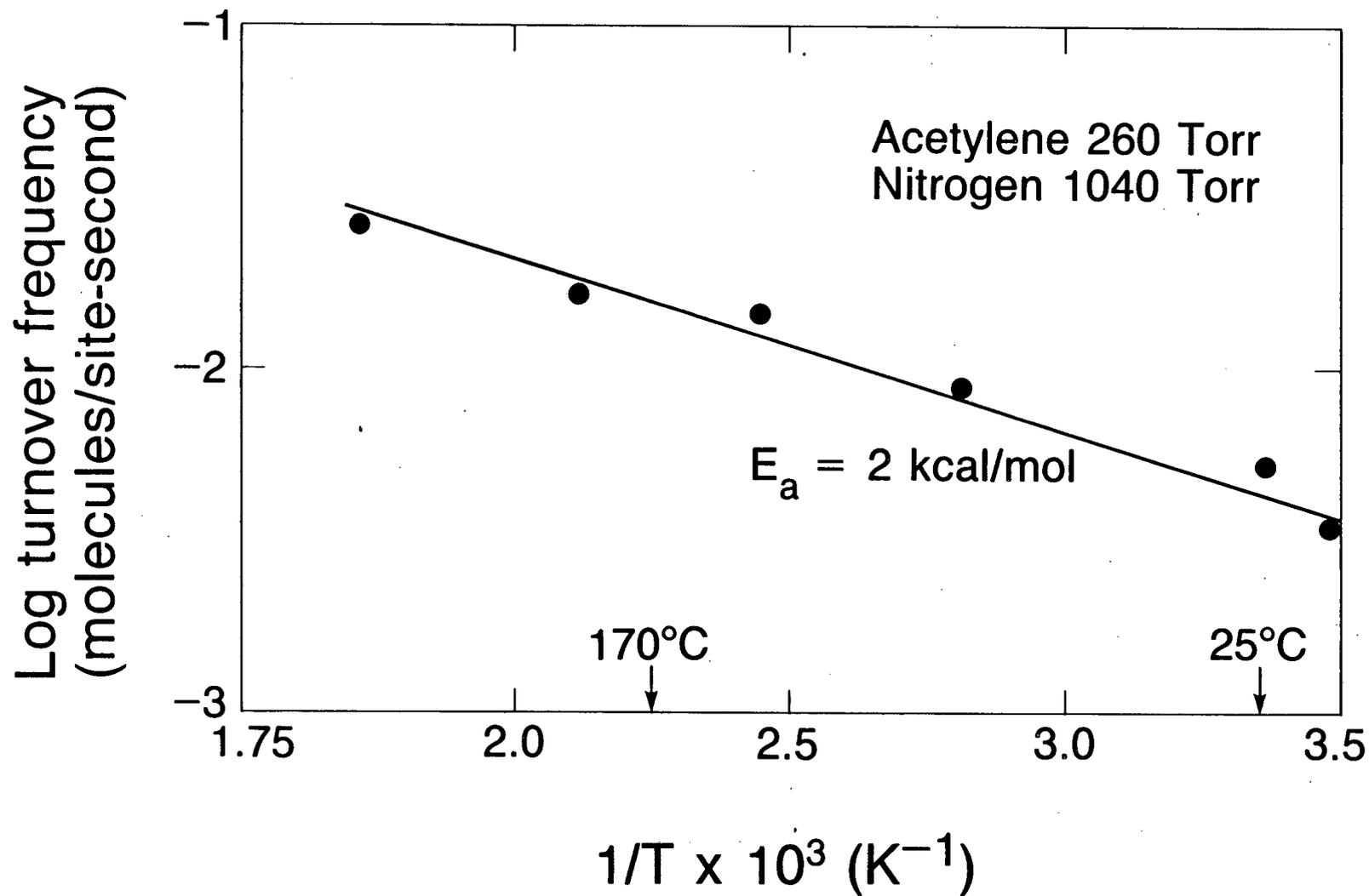
XBL 856-11203

FIGURE 3



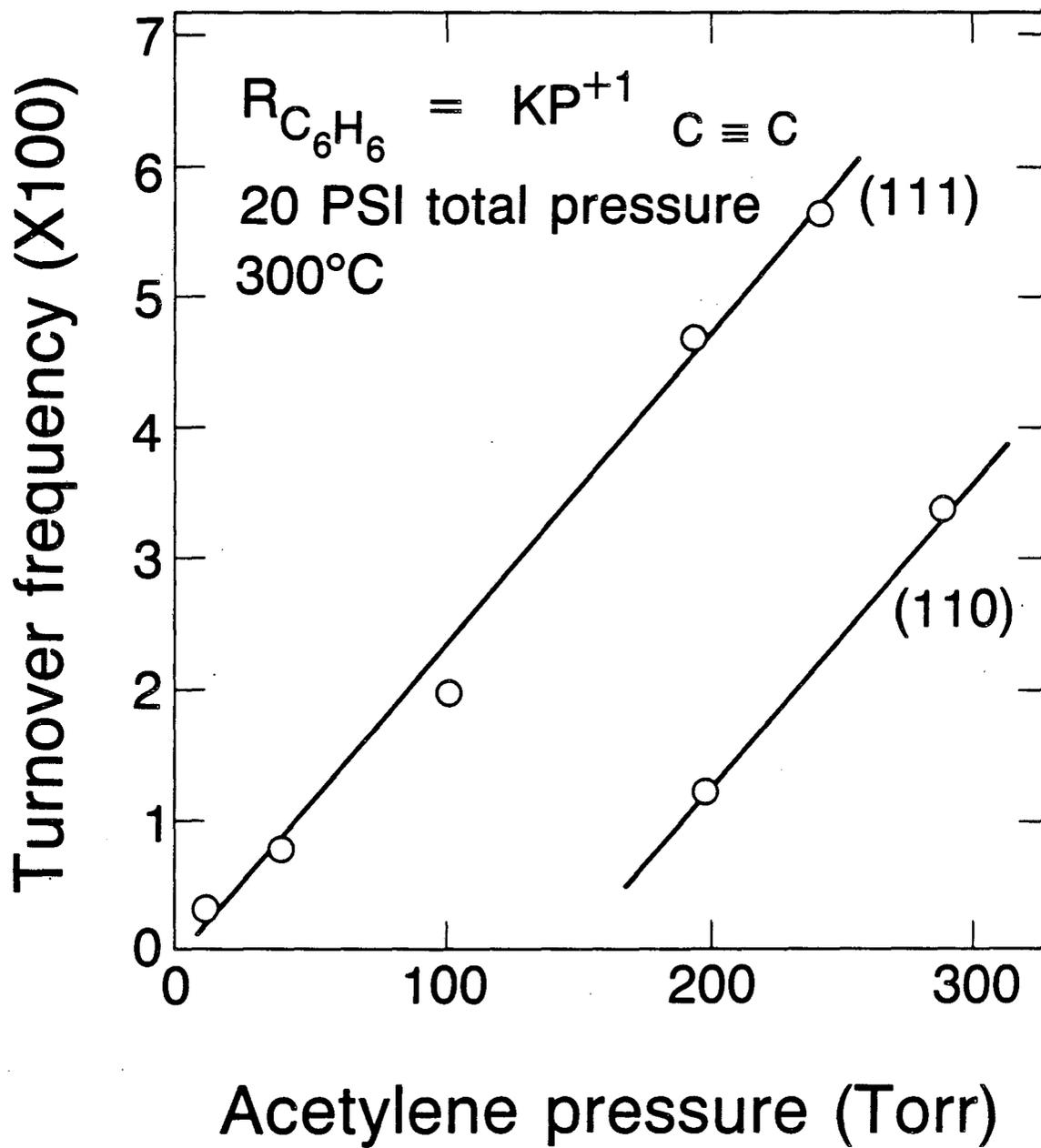
XBL 856-11212

FIGURE 4



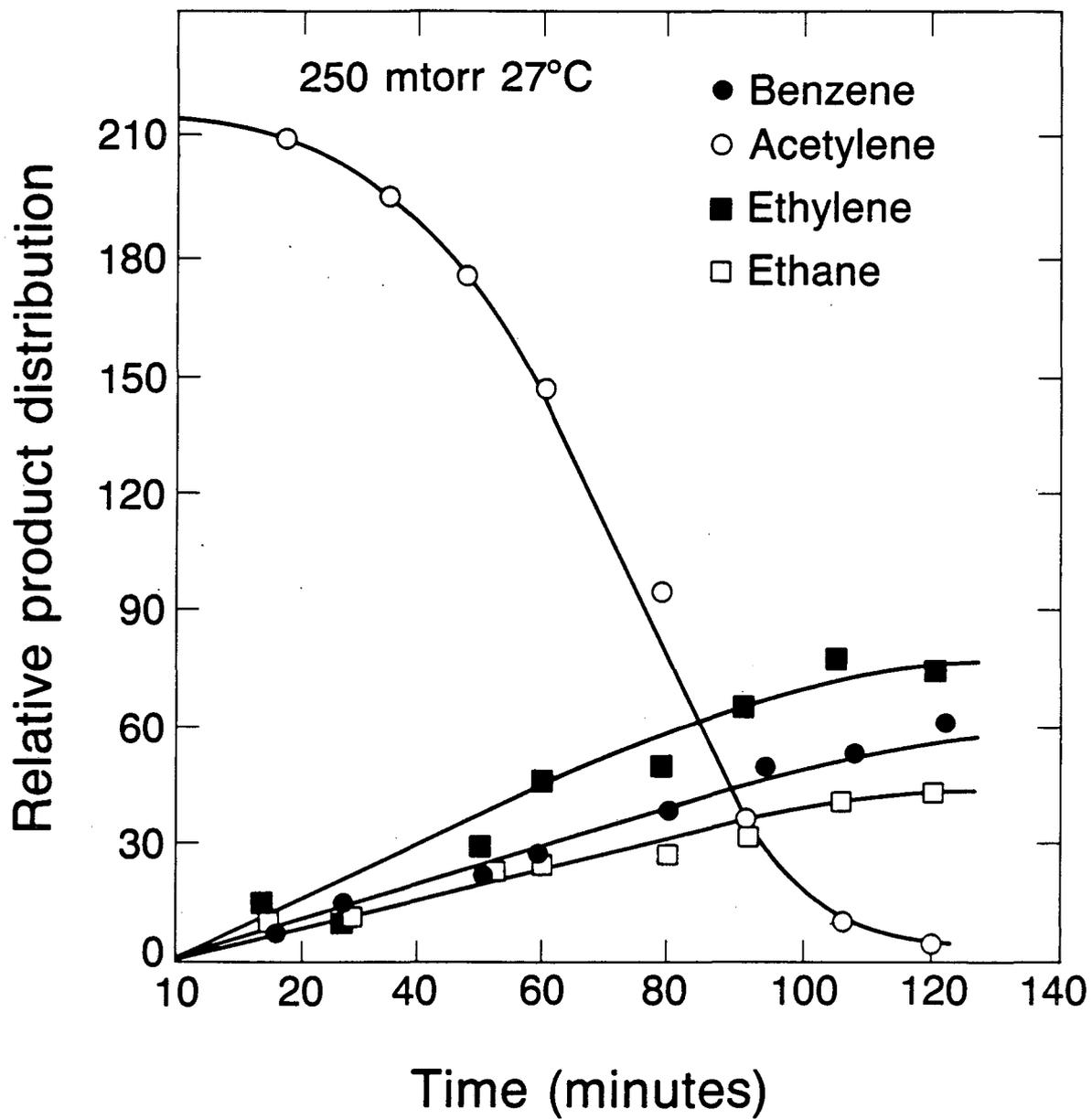
XBL 856-11199

FIGURE 5



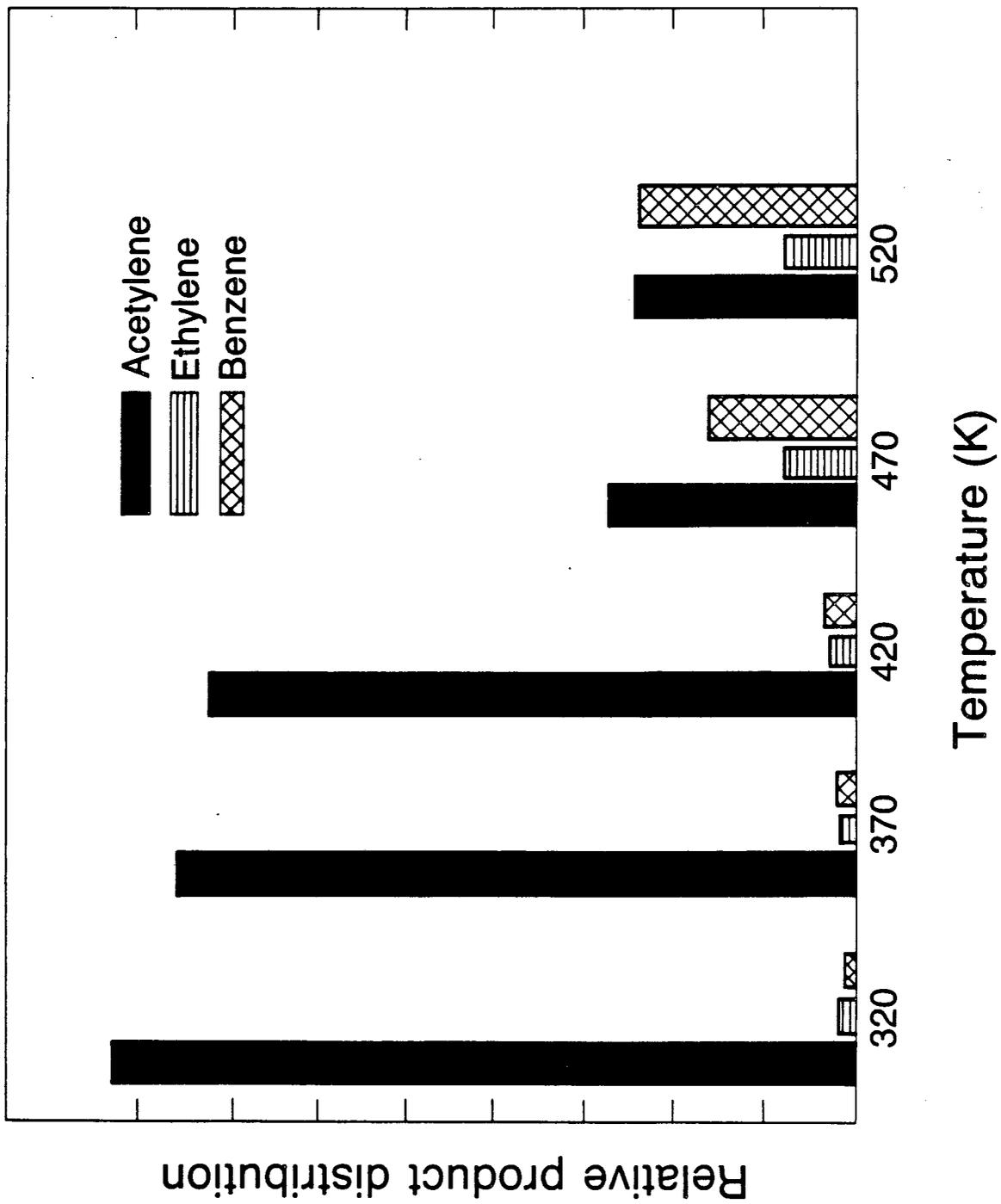
XBL 856-11196

FIGURE 6



XBL 856-11195

FIGURE 7



XBL 856-11213

FIGURE 8

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*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*