Title

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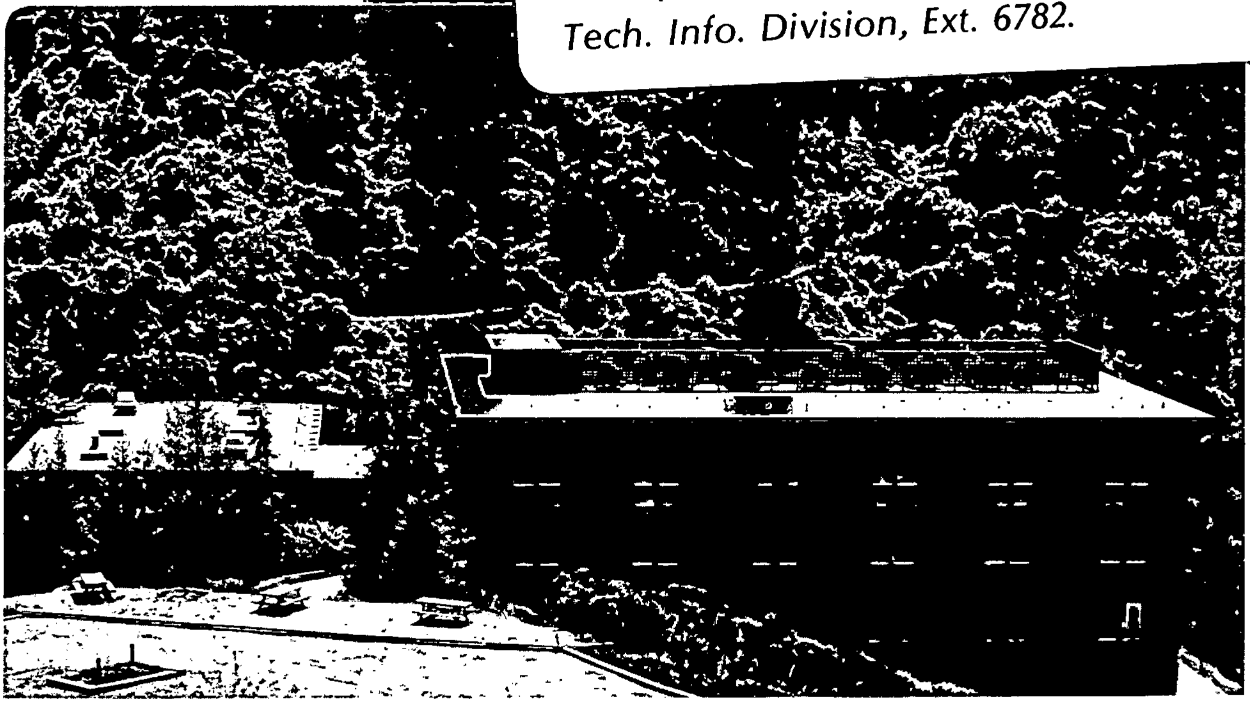

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THE EFFECT OF POTASSIUM ON THE CATALYZED REACTIONS OF n-HEXANE OVER Pt (111) SINGLE CRYSTAL SURFACES

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Abstract

The effect of potassium on the n-hexane conversion catalyzed by Pt(111) single crystals has been studied near atmospheric pressures. Reaction activity, selectivity and self-poisoning with time were studied as a function of potassium coverage of the crystal faces. The activity of the catalyst dropped drastically with as little as 2% potassium atoms on the surface, with no improvement in selectivity or stability. The temperature dependence in the range 550K-625K of the reaction rates was not significantly different from the clean platinum case.

The changes in the structure of the carbonaceous deposits formed during the reaction have also been studied. The amount of carbon on the surface after reactions was higher on the platinum surface that was covered with 2% potassium atoms, as compared with the clean platinum case. The amount of bare platinum available for reaction, however, increase by a factor of two. When potassium was added to the platinum surface, the carbonaceus deposits showed a higher hydrogen content,

with a higher activation energy for its desorption, an increase up to 4 Kcal/mole more than for the clean platinum case. The inhibition of the dehydrogenation of adsorbed hydrocarbon species in the presence of coadsorbed potassium on the platinum surface explain the changes of reactivity that are reported.

Introduction.

Alkali metals are frequently employed as promoters in the preparation of practical metal catalysts. Potassium is a well known additive to iron for ammonia synthesis [1] and to catalysts for the hydrogenation of carbon monoxide [2]. While the promoting effect of the elements like Ca, B, Al, Si, Ga and Bi on platinum reforming catalysts have been studied [3,4,5], the influence of alkali metals on the activity and selectivity of platinum for hydrocarbon conversion reactions has been studied to a much lesser extent. A recent patent reported enhanced cyclization selectivity over Na_2O promoted platinum catalysts [6].

The effect of potassium on the flat Pt (111) single crystal surfaces on n-hexane conversion is reported here. The activity of the promoted catalyst was lower by a factor of two for all reactions when a small coverage ($\Theta_K \sim 0.05$) of the alkali metal was deposited on the platinum surface. This decrease in reactivity was accompanied by increased self-poisoning. The temperature dependence of the reaction rates was unaltered by the presence of potassium on the platinum surface in the 550-625K temperature range. The effect of oxygen on the catalysts was independent of that of potassium: while potassium decreased the overall activity, oxygen enhance hydrogenolysis.

A slightly larger amount of carbon, measured by Auger Electron Spectroscopy, was seen when about 2% K atoms were present on the catalyst surface (as compared with the clean platinum case). This increase, however, was accompained by an increase of the bare platinum area available for catalytic activity. Also the H/C ratio of these carbonaceous deposits was higher in the presence of potassium. All this suggests a more three dimmensional structure of the hydrocarbon fragments adsorbed, with less carbon to metal bonds. An inhibition of the dehydrogenation activity of platinum in the presence of potassium explains these results.

Experimental.

All of the experiments were carried out in an low pressure-high pressure apparatus designed for combined surface analysis and catalytic studies using small area catalyst samples, as described previously [7]. The system is equipped with four-grid electron optics for Low Energy Electron Diffraction (LEED) and Auger Electron Spectroscopy (AES), an ion gun for crystal cleaning, a quadrupole mass spectrometer, and a retractable internal isolation cell that constitutes part of a microbatch reactor in the 10^{-2} - 10 atm pressure range. The reaction cell and external recirculation loop were connected to an isolatable pressure gauge, a circulation pump, and a sampling valve connected to a gas chromatograph, used to follow the hydrocarbon conversion.

Platinum single crystals (99.998% purity) were cut to the (111) and 6(111)x(111) orientation within one degree (and less than 1mm thickness) using a standard procedure. They were spotwelded to a rotatable manipulator, as described previously [8]. Both crystal faces were cleaned by repeated argon ion sputtering, oxygen treatment, and annealing, until a well defined LEED pattern was obtained, and no Ca, Si, P, O, S or C were detected by AES. Research purity n-hexane (Phillips, >99.99% purity), and hydrogen (Matheson, >99.99%) were used as supplied.

A Saes Getters potassium source was mounted about 4 cm from the sample surfaces, giving deposition rates on the order of 0.1 monolayers/min. The amount of potassium on the surface was measured by AES. The relationship between the K AES signal and the coverage was obtained using potassium uptake curves, as described in detail elsewhere [9]. This relationship can be written as $K_{251}/Pt_{237}=6.1\ \theta_K + 0.3$ (20%) where K_{251} and Pt_{237} are the signal intensities of the Auger 251 eV and 237 eV transitions of potassium and platinum respectively, and θ_K is in fraction of a monolayer (one monolayer is equivalent to 5.4×10^{14} potassium atoms per square centimeter).

After cleaning the crystal, the desired amounts of potassium were deposited either by controlling the deposition time, or by depositing excess potassium and flashing the crystal at a fixed temperature to desorb part of it . Since the base pressure of the system was of the order of $\leq 1\times10^{-9}$ torr, oxygen and water adsorption could not be completely avoided. The effect of this coadsorbed oxygen will be discussed in more detail later.

For performing an experiment, the reaction cell was closed, imbeding the crystal into the high pressure loop. n-Hexane vapor and hydrogen were then introduced to the desired pressures, circulation was commenced, and the crystal was heated to the reaction temperature. The reaction temperature was continuosly regulated to ± 2K using a precision temperature controller refered to a chromel-alumel thermocouple spot-welded to a face of the crystal. The product formation was followed by gas chromatography. Since the high pressure loop acts as a well mixed batch reactor, the data is obtained in a form of product accumulation as a function of time. Initial rates were calculated from the slope of these curves at the initial time, and they were reproducible within 30%. Selectivities, calculated for the accumulated products after two hours, were reproducible within about 5%.

After the reactions were performed, the loop was pumped down with a sorption pump to below 10^{-3} torr, the cell was opened, exposing the crystal to ultra high vacuum, whereupon Auger spectra were immediately recorded. Then, CO adsorption - desorption or hydrogen desorption experiments were carried out. For the titrations of the available bare platinum surface area by CO adsorption, the sample was flashed up to about 500K to desorb any reversibly adsorbed molecules, and then exposed to 36L of CO (1L = 10^{-6} torr.sec). Finally, thermal desorption spectra (TDS) were recorded with the mass spectrometer tuned at m/e = 28. In the case of the hydrogen desorption experiments, TDS were recorded with m/e = 2 immediately after the Auger spectra were taken.

Results.

n-Hexane conversion on the Pt(111) face in the presence of coadsorbed potassium.

The rates of hydrogenolysis, isomerization, cyclization and aromatization of n-hexane were investigated over the flat (111) platinum surfaces. The gas mixture used for these reactions were 20 torr n-hexane and 600 torr of H_2, and the reactions were carried out at 573K unless indicated otherwise. Product accumulation curves, determined as a function of reaction time for the (111) surface and different potassium coverages, are shown in figure 1. From these, initial reaction rates, selectivities (as a percentage of desired accumulated product over the total conversion), and extent of self-poisoning (as the rate after two hours over initial rate), were obtained; they are shown in figures 2, 3 and 4 respectively. All four reactions are strongly inhibited when only a small amount of potassium is present on the surface: about 5% of a monolayer potassium reduces the total activity to one-half to that on clean platinum. The selectivities for the different products did not change much, and, considering the large decrease in overall activity, these changes were not significant. Selfpoisoning of all the reactions became enhanced with the addition of potassium.

The temperature dependence for hydrogenolysis, isomerization and cyclization reaction rates were studied in the temperature range between 550K and 675K for clean platinum and for platinum with $\theta_K = 0.05$ potassium coverage. The activation energies obtained for the low temperature region (550K-625K) are sumarized in table I; they were the same within experimental error, for the clean and potassium covered platinum surfaces. In the high temperature region, there was a drop in activity from what was expected by the Ahrrenius expression for both cases with and without potassium. However, This drop was more pronounced in the case of the potassium covered surface.

The dehydrogenation of n-hexane to olefins under the same conditions was also studied. The respective product accumulation curves are shown in figure 5. Since olefin formation is much faster than the other reactions, initial reaction rates could not be accurately determined. It can be, howevwe, seen that the potassium coverage was not too important in this case. The total accumulated olefin after 30-60 minutes of reaction droped to about one half with a potassium coverage of $\Theta_K = 0.45$, as compared with $\Theta_K = 0.05$ for the other reactions. Also, a maximum in the accumulated product curves as a function of time was present at high potassium coverages ($\Theta_K \geq 0.3$), after approximately 60 minutes of starting the reactions.

Studies were performed also on the 6(111)x(111) stepped platinum surface and the results were qualitatively the same as those obtained on the Pt(111) crystal face. However, more work needs to be carried out to make a quantitative comparison between those two surfaces.

Morphology of the carbonaceous deposits formed during n-hexane reactions.

Auger analysis of the surface composition following the n-hexane reaction studies always revealed the build-up of about a monolayer of strongly bonded carbonaceous deposits. No ordering of this layer could be detected by LEED. The self-poisoning of all reactions strongly suggest that at least part of these carbonaceus species were bonded irreversibly as a deactivating residue. Figure 6 shows the 273 eV carbon to 237 eV platinum Auger transitions signal ratio (C_{273}/Pt_{237}), measured following reactions as a function of potassium coverage. These peak height ratios can be converted into approximated ($\pm$ 25%) atomic ratios, expressed as carbon equivalents per surface platinum atom, by multiplying them by 0.62 [10]. As we can see, there was a slight increase in the amount of carbon deposited up to $\theta_K \sim 0.3$, followed by a decrease by a factor of three at high potassium coverages, probably due to potassium atoms blocking the platinum sites.

The fraction of platinum surface that remains clean after the n-hexane reactions was measured using a CO titration technique described in detail previously [11]. The CO thermal desorption spectra obtained from these titrations are shown in figure 7 for different potassium coverages. The temperature of the maxima and the shape of the spectra followed the expected tendency for CO adsorption on potassium precovered platinum surfaces [12], i.e., the binding energy of CO to platinum increased in the presence of coadsorbed potassium. The area under each spectra is proportional to the amount of CO desorbed, that is also proportional to the fraction of uncovered platinum surface. In this way we were able to measure the fraction of bare platinum after reactions as a function of potassium coverage, since CO does not adsorb on potassium under our experimental conditions. The results are shown in figure 8. Inspite of the scattering in the data, there was a clear increase of this fraction up to about $_K = 0.3$, followed by a decrease as potassium covers up a larger fraction of the platinum surface.

Energetics of the C-H bond breaking.

Hydrogen thermal desorption spectra were also recorded following the n-hexane reactions. These are shown in figure 9 for different potassium coverages. The spectra represent the sequential dehydrogenation of the strongly adsorbed species that were deposited by the reaction mixture. The desorption takes place in at least two steps, with broad peaks around 500K and 650K. As discussed in a previous paper [13], the first desorption peak mainly corresponds to -hydrogen abstraction, while the second peak represents the decomposition of CH fragments and breaking of C-H bonds with no easy access to metal sites.

The area under these spectra are proportional to the amount of hydrogen in the carbonaceous deposits. They can be converted to approximate hydrogen to carbon ratios using the AES carbon signal and a benzene adsorption calibration [5]. There is a rapid increase in the H/C ratio with increasing potassium coverage, up to ˆ $_K \sim 0.08$, followed by a slower one thereafter.

The activation energy for the hydrogen desorption by -elimination could also be calculated assuming first order desorption kinetics [13]. The potassium coverage dependence of these activation energies is shown in figure 10. Starting at about 26 Kcal/mole for the clean platinum surface, a sharp increase of about 2 Kcal/mole when $\theta_K \sim 0.02$ is seen, followed by a further increase of other 2 Kcal/mole at ˆ $_K \sim 0.45$.

Preliminary n-hexane adsorption experiments in ultra high vacuum conditions have also been performed. Since the n-hexane adsorption is dissociative and activated, the results of these studies have to be analyzed cautiously. The n-hexane uptake curves at any given temperature, measured as the amount of carbon on the surface as a function of n-hexane expossure, showed less adsorption for the potassium precovered surface compared with the clean platinum case (by about a factor of five). This adsorbed hydrocarbons had a higher H/C ratio in the case of the potassium precovered surface, as in the high pressure experiments. Rehydrogenation of the adsorbed species deposited under UHV conditions were performed by exposing the catalyst to 600 torr H_2 pressure and the same depositing temperature for 5-10 minutes, showing that the fraction of irreversibly adsorbed carbon was always greater than 60%.

Effect of coadsorbed oxygen on the reactivity of the potassium-platinum system.

It is well known that alkali metals greatly increase the sticking probability of molecular oxygen and water. The base pressure of our system, about 10^{-9} torr, did not allow us to keep clean metallic potassium in most of the runs, and more than half of the AES showed the presence of oxygen traces before the reactions. In any case, after inserting the sample in the high pressure loop, a higher background pressure (more than 10^{-3} torr) provides enough water for the oxygenated species to form: oxygen was always found present after each run. To check the effect of this oxygen on the reactions, some experiments were carried out in wich the K/Pt samples were pretreated with oxygen prior to the reaction. We also studied the catalytic activity of a platinum surface that was preoxidized and then covered with $\Theta_K = 0.03$ potassium. The results are sumarized in table II. Except for an increase of hydrogenolysis activity with oxygen, all potassium-platinum systems had comparable chemical performances. The increase in hydrogenolysis activity has been observed previously for platinum oxide alone and for calcium oxide on platinum [5].

Discussion.

The main effect of the addition of potassium on the platinum catalyst surface is to markedly inhibit the n-hexane conversion. It not only reduces the initial rates for the different reactions, but also increases slightly the self-poisoning rate of the catalyst, that is, the rate of decrease of the activity with time. However, the self poisoning can not be directly related to the presence of carbonaceous deposits because, although there was more carbon present on the surface after the reactions when the catalyst was predosed with potassium, there was also a larger area of uncovered platinum available for the catalytic reaction. Other important characteristics of these carbonaceous deposits were the higher hydrogen content and the higher activation energy for C-H bond breaking. These properties are consistent with the ones obtained for n-hexane adsorbed under ultra-high vacuum conditions.

As we already mentioned, potassium as an additive causes the strong decline of the n-hexane conversion reaction rates, even at potassium coverages as low as $\theta_K = 0.03$. The change of catalytic activity versus potassium coverage showed a pronounced non linearity (The initial rates are roughly proportional to $\theta_K^{-1/3}$). This suggest that electronic, and not structural changes on the surfaces caused by site blocking by potassium, are responsible for the differences observed.

Alkali metals are well known as electron donnors on almost all metalic surfaces. One of the most extended uses of this property is in the fabrication of low work function photocathodes [14]. The same effect is believed to be responsible for the enhanced activity of the ammonia synthesis [1] and the Fisher-Tropsch [2] catalysts when alkali metals are used as promoters. The CO/K/Pt system has been carefully characterized recently in our laboratory using surface sensitive techniques: Thermal Desorption Spectroscopy (TDS), High Resolution Electron Energy Loss Spectroscopy (HREELS), and Ultraviolet Photoelectron Spectroscopy (UPS) [12]. A large change of the electronic properties of platinum when potassium was adsorbed on the surface was observed, as inferred from the following two main results: an increase in activation energy of the CO desorption from 25 to 36 Kcal/mole with $\theta_K = 0.5$ (manifested by a 210K shift in the desorption peak maximum of the CO TDS); and a decrease in the C-O vibrational frecuency, down to 1400 cm^{-1} at $\theta_K = 0.3$ and low CO coverages, the lowest ever reported for CO bonded to a metal. Also in the same work, a drop of about 4 eV in the work function of the metal at $\theta_K = 0.3$ was reported.

Due to the complexity of the hydrocarbon system, some simplifications are needed before attempting to explain our results. To start with, we will adopt the two step mechanism for hydrocarbon conversion initially proposed by Cimino et. al. [15]. According to this scheme, after the dissociative adsorption of the reactants, a further dehydrognation of the adsorbed hydrocarbons takes place. These dehydrogenated intermediates then rearrange and desorb as products. In this mechanism, the slow step can be, depending on the conditions of the reaction, either the dehydrogenation or the rearrangement of the adsorbed intermediates. Since different reactions need different intermediates, while potassium was found to be a non-selective poison, it seems that the presence of potassium on the platinum surface slows down the dehydrogenation steps, and therefore, we propose that dehydrogenation is the limiting step under our conditions.

The low pressure experiments on n-hexane adsorption showed a decrease in the apparent sticking coefficient with potassium on the surface. In this process, at least one C-H bond breaking takes place, followed by the formation of a carbon-metal bond of the dissociated molecule. qualitative calculations [16,17], photoemission studies of energy level shifts [18], and work function changes [19,20] all suggest that this adsorption is accompanied by a charge transfer from the hydrocarbon to the platinum, leaving the former with a carbonium ion character. Potassium on the surface, acting as an electron donnor, will then inhibit this charge transfer, making the process less favorable. This effect should be more accentuated as the hydrocarbon dehydrogenates further, because the remaining hydrocarbon fraction is less able to interact with the extra negative charge provided by the potassium. This may be the reason why, while n-hexane adsorption at low pressures is severely inhibited with potassium, there is not much change in the dehydrogenation reaction rates, where high hydrogen pressures keep the species adsorbed on the surface hydrogenated to a greater extent. Only when dealing with the isomerization, cyclization, and hydrogenolysis reactions, that requires more dehydrogenated intermediates, the poisoning effect of potassium is appreciable.

A further piece of information that supports the preceeding conclusion is the steep rise in the activation energy for hydrogen β elimination of the carbonaceous deposits shown in figure 10. As in the adsorption experiments, potassium makes breaking the C-H bonds of the adsorbed species more difficult.

The morphology of the carbonaceous deposits formed during the reactions also changes with potassium on the surface. Although there is a slight increase in the carbon coverage up to $\theta_K \sim 0.04$, as shown in figure 6, this is accompanied by an increase, and not a decrease, in the fraction of uncovered platinum surface (fig. 8). This can be explained as follows: less multiple site adsorption yields less hydrogenolysis and C-C bond breaking activity, leaving more adsorbed species on the surface, as shown by a higher amount of carbon in fig. 6. However, these carbonaceous deposits do not block much of the platinum surface, because there are fewer carbon-metal bonds involved (less multiple adsorption); the molecules are "sticking out" instead of "lying down" on the surface, giving more 3-dimensional character to the deposits [11]. This also implies a higher hydrogen to carbon ratio of the adsorbed species, as observed.

The effect of adsorbed alkali metals and the electronic changes they induce on platinum surfaces have been studied by other researchers. Foger and Anderson [21] studied the effect of different additives on the Pt/Y-zeolite catalyst for neopentane conversion. The electron deficiency of the platinum particles, measured by ESCA, was founded to follow the sequence La-Y>Ca-Y>Na-y zeolite. At the same time, the total activity for the neopentane conversion decreased in the same order. Since neopentane does not have secondary or tertiary carbon atoms, it is expected to react only on the metal. Their work is then in accordance with our results, namely, the activity for hydrocarbon conversion slows down with an increase in electron density of the platinum catalyst.

Finally, a patent [6] reports an activity enhancement of a factor of three for benzene formation from n-hexane when few ppm of sodium were added to a carbon supported platinum catalyst. One possible explanation for the difference with our work is that, while sodium forms alloys with platinum, potassium remains as a separate phase (preferentially on the surface), and desorbs above ~ 1000K [22]. Consequently, different electronic interactions between the alkali metals and platinum are to be expected, which change the catalytic behaviour of the two systems.

Some of our results remain unexplained. The temperature dependence of the reaction rates in the range of 600-675K showed a decrease in activity as compared with that expected from the Ahrrenius expression. This can be attributed to an increase in coke formation at higher temperatures, that poisons the platinum activity. However, it is not clear at this point why potassium will accelerate this effect, as observed experimentally. Also we cannot readily explain why the olefin accumulation curves showed a maximum at high potassium coverages. The fact that the total amount of olefin prodeced decreases with time means that they are reacting to form other products, but it is not clear why potassium favors these side reactions.

Acknowledgment

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Figure captions.

Fig 1. Product accumulation curves as a function of time for n-hexane reactions over Pt (111) surfaces, dosed with different amounts of potassium: a) Hydrogenolysis, b) Isomerization, c) Methylcyclopentane formation (cyclization) , d) Aromatization.

Fig 2. Initial reaction rates for hydrogenolysis, isomerization, cyclization, and aromatization of n-hexane over Pt (111) surfaces as, a function of potassium coverages.

Fig 3. Selectivity of accumulated products after two hours of n-hexane reaction over Pt (111) as a function of potassium coverages.

Fig 4. Stability to self-poisoning, expressed as the ratio of reaction rates after two hours over initial rates, for hydrogenolysis, isomerization, cyclization and aromatization of n-hexane over Pt (111) surfaces as a function of potassium coverages.

Fig 5. Product accumulation curves as a function of reaction time for n-hexane dehydrogenation over Pt (111) surfaces covered with different amounts of potassium.

Fig 6. Carbon to platinum AES signal ratio after n-hexane reaction over Pt (111) surfaces as a function of potassium coverages.

Fig 7. CO thermal desorption spectra following CO saturation of the Pt (111) surface after two hours of n-hexane reaction for different potassium coverages. The adsorption temperature was 300K-310K, the heating rate 80 K/sec.

Fig 8. Fractional concentrations of uncovered platinum surface sites after n-hexane reactions determined by CO titration, as a function of potassium coverage (relative to the same fractional concentration after reaction for the clean platinum case).

Fig 9. Hydrogen thermal desorption spectra of the carbonaceous deposits after n-hexane reactions over Pt (111) surfaces with different potassium coverages. Heating rate = 80 K/sec.

Fig 10. Activation energy of the hydrogen β - elimination from the carbonaceous deposits after n-hexane reactions over Pt (111) surfaces as a function of potassium coverages.

Table I

Activation energies for n-hexane reactions over clean and potassium dossed Pt (111) surfaces in the 550K - 625K temperature range.

Reaction	Activation energy E_a (Kcal/mole)
Hydrogenolysis	29 ± 3
Isomerization	56 ± 5 → 25 ± 3
Cyclization	33 ± 3

Table II

Effect of oxygen on clean and potassium precovered Pt (111) surfaces for n-hexane conversion (T=573K, P_{HC} = 20 torr, P_{H_2} = 600 torr).

Surface	Θ_K	O/Pt AES[a]	Initial rates[b] Hydrogenolysis	Isomerization	Cyclization
Clean Pt	0	0	14	17	19
K/Pt	0.02	~ 0	3	6	6
K/Pt	0.03	~ 0	4	5	6
K_xO/Pt[c]	0.02	0.08	11	5	8
K/PtO[d]	0.03	0.28	12	6	6

a Ratio of the 515 eV and 237 eV Auger transition signals of oxygen and platinum respectively.

b rates in n-hexane molec/Pt atom.sec (x10^3) (± 20%).

c Saturated with oxygen at room temperature after potassium deposition.

d Potassium deposited after preoxidizing the platinum surface at about 1000K.

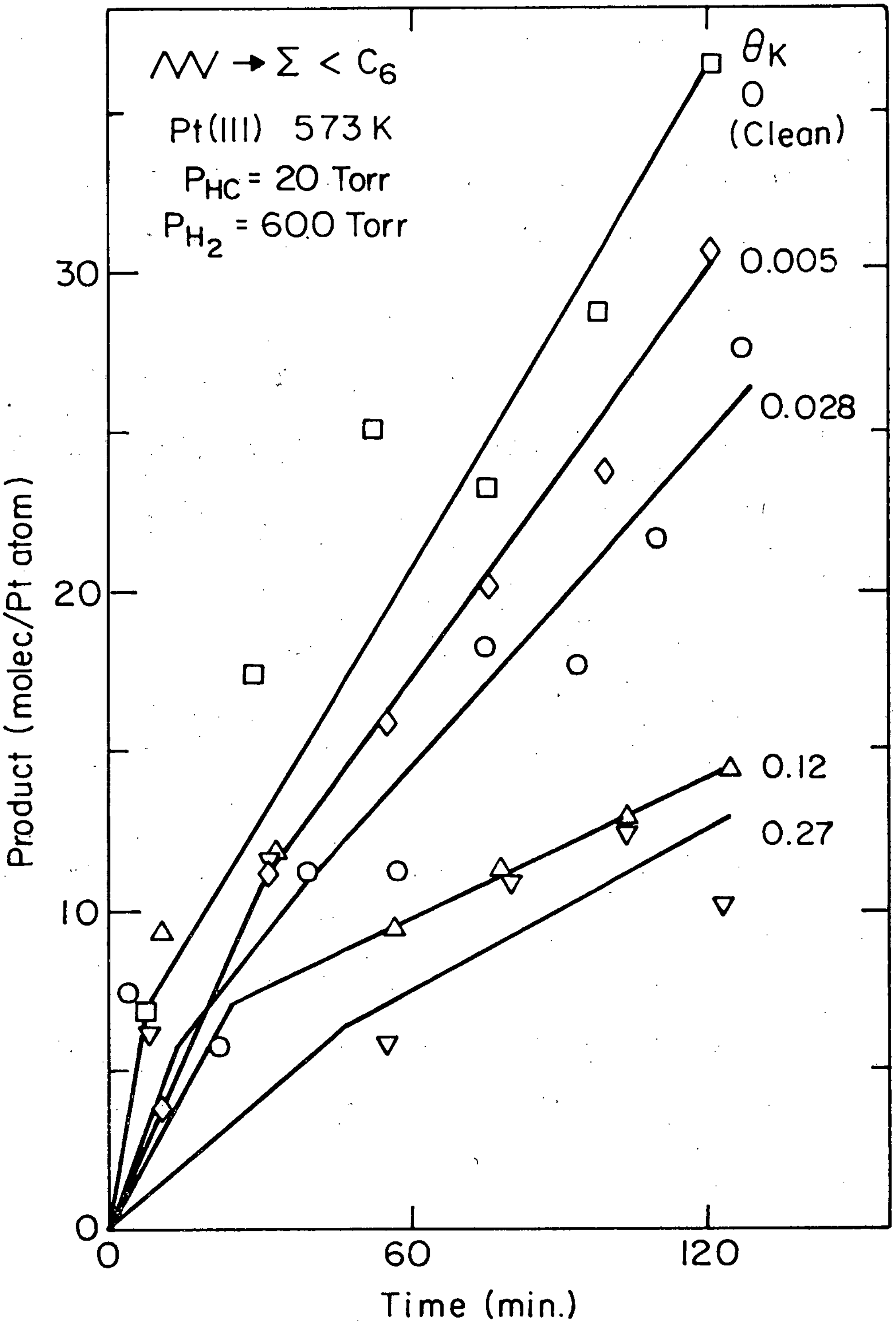

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Fig. 1a

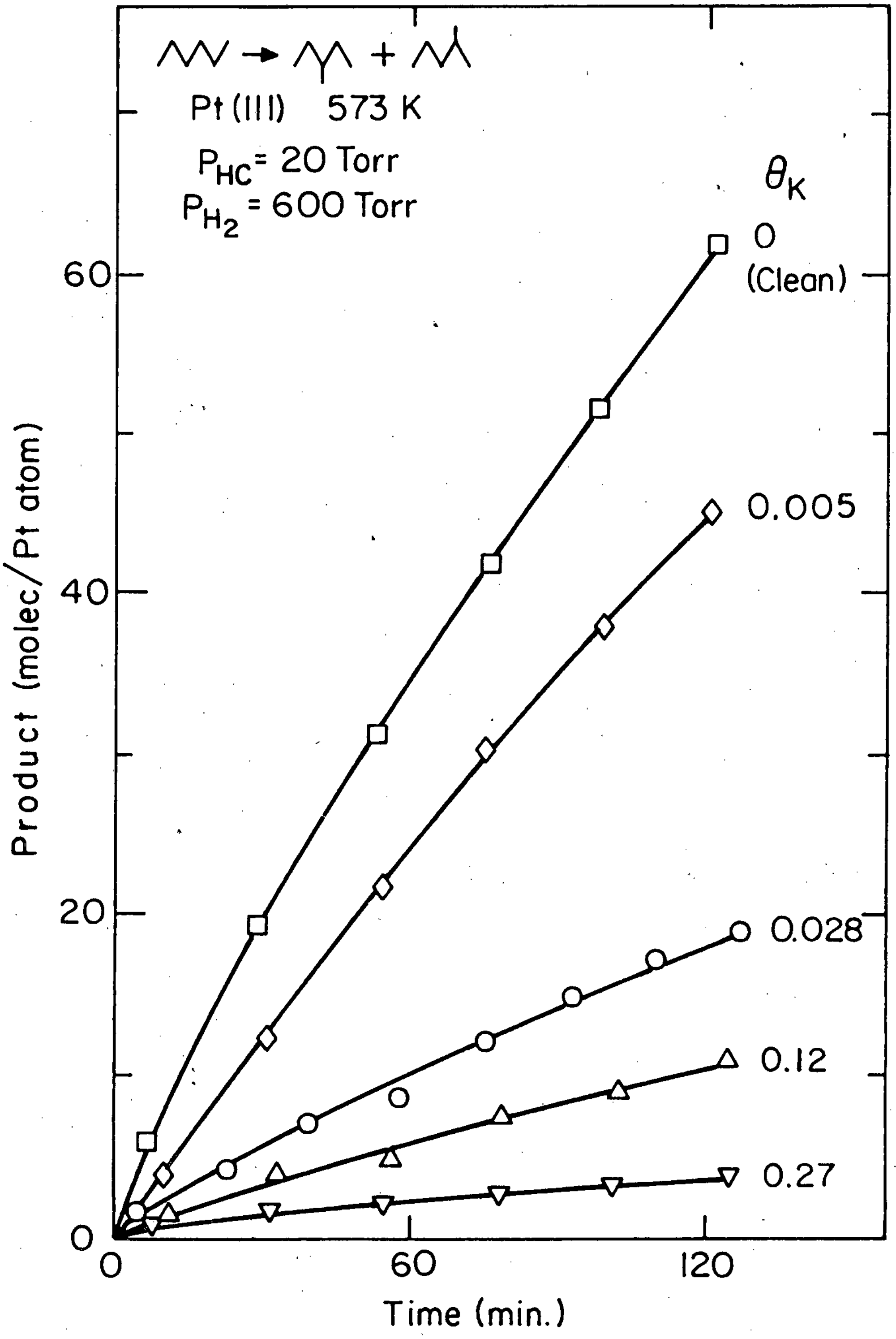

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Fig. 1b

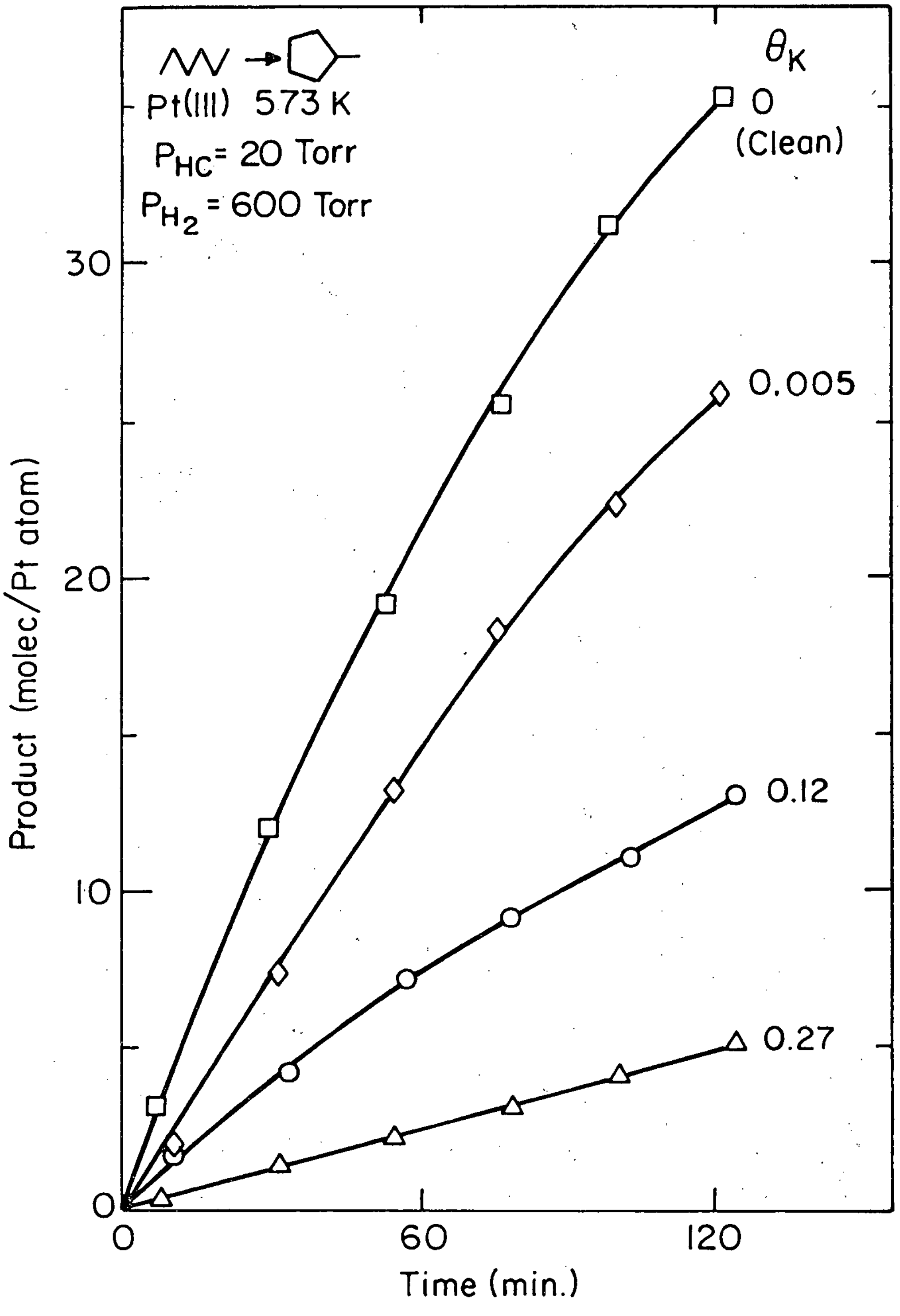

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Fig. 1c

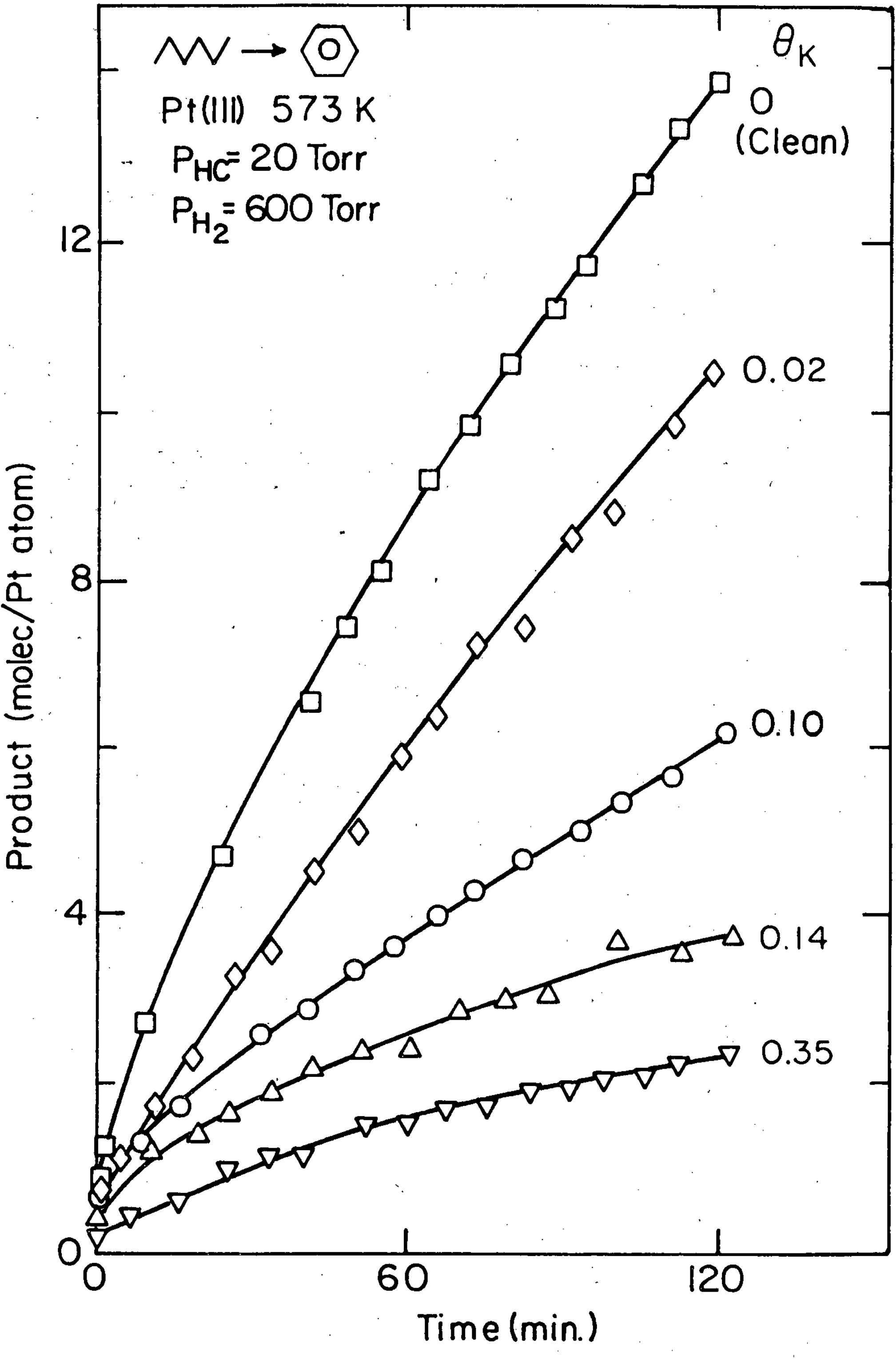

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Fig. 1d

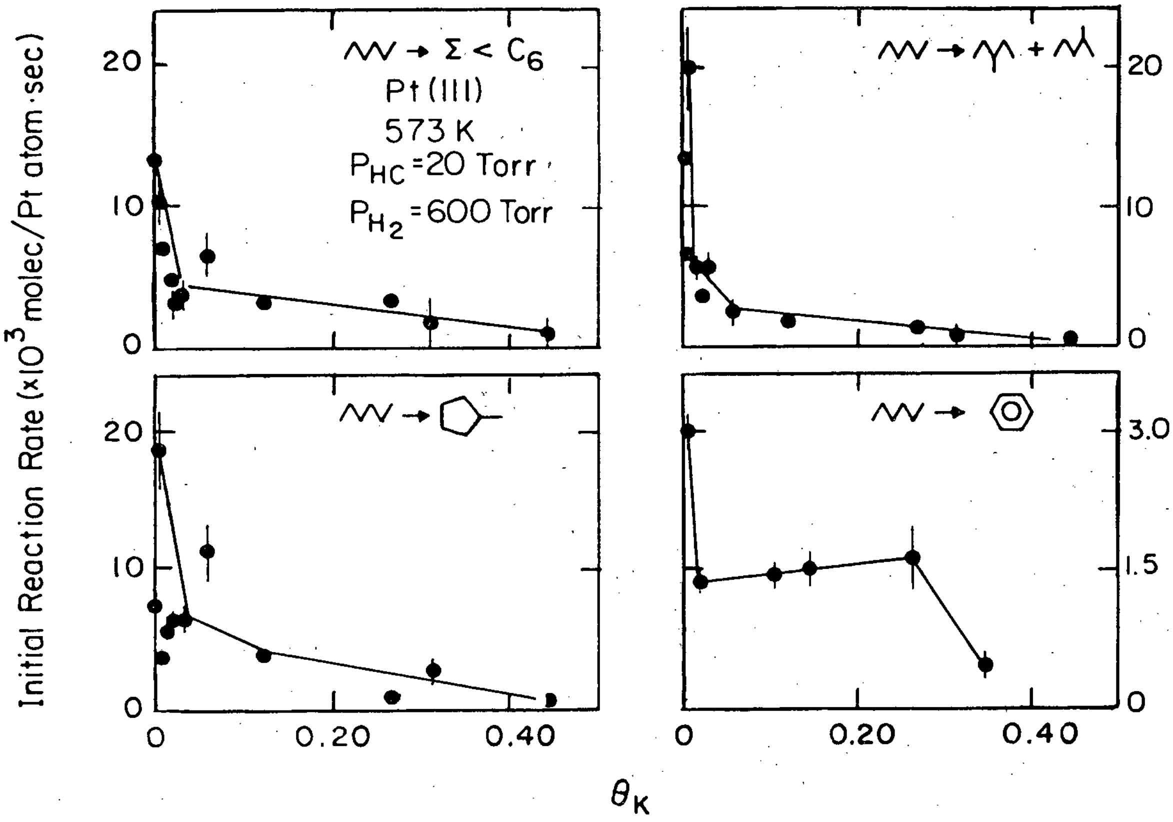

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Fig. 2

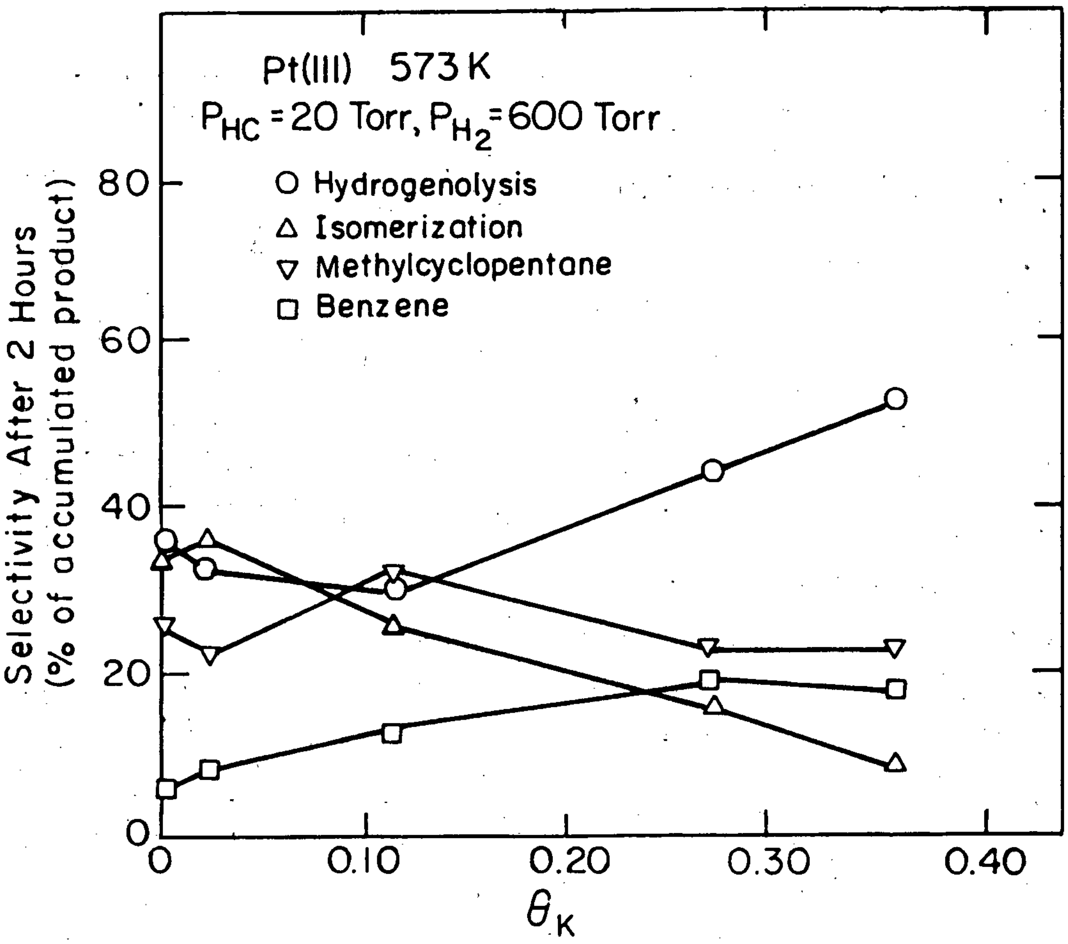

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Fig. 3

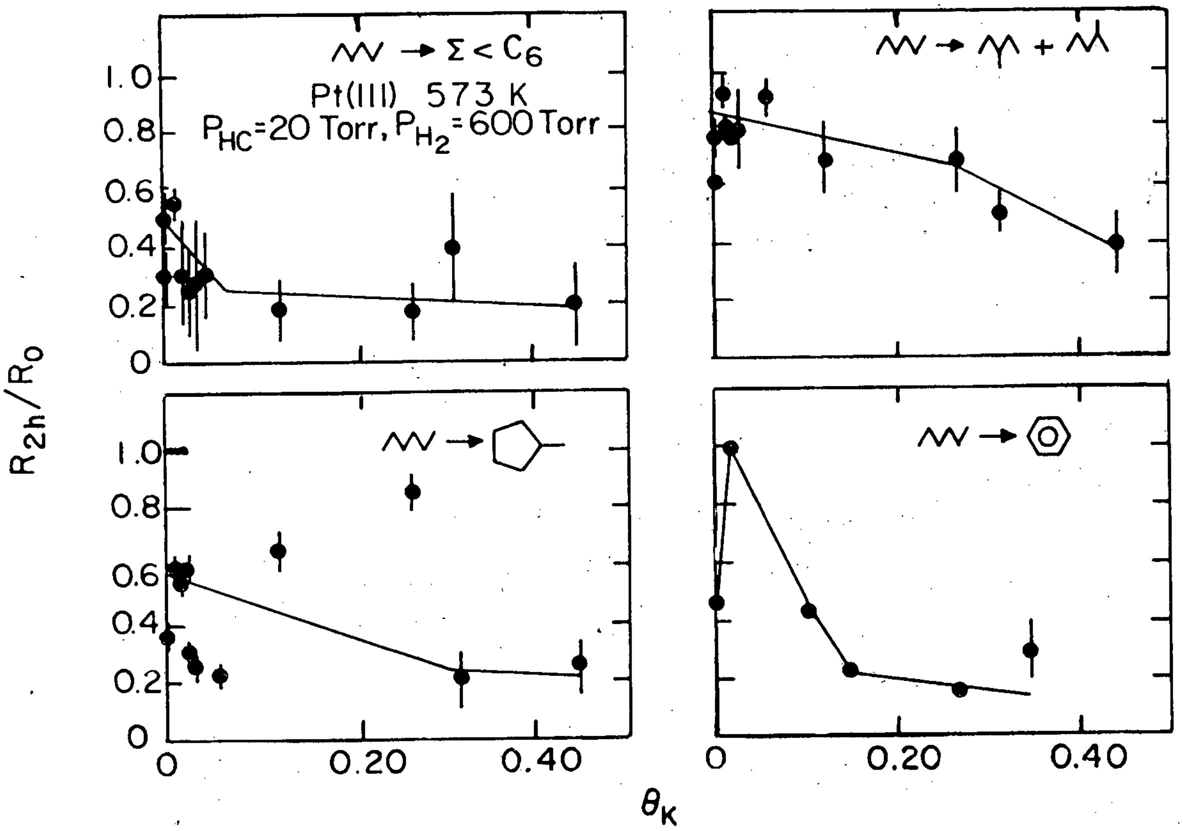

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Fig. 4

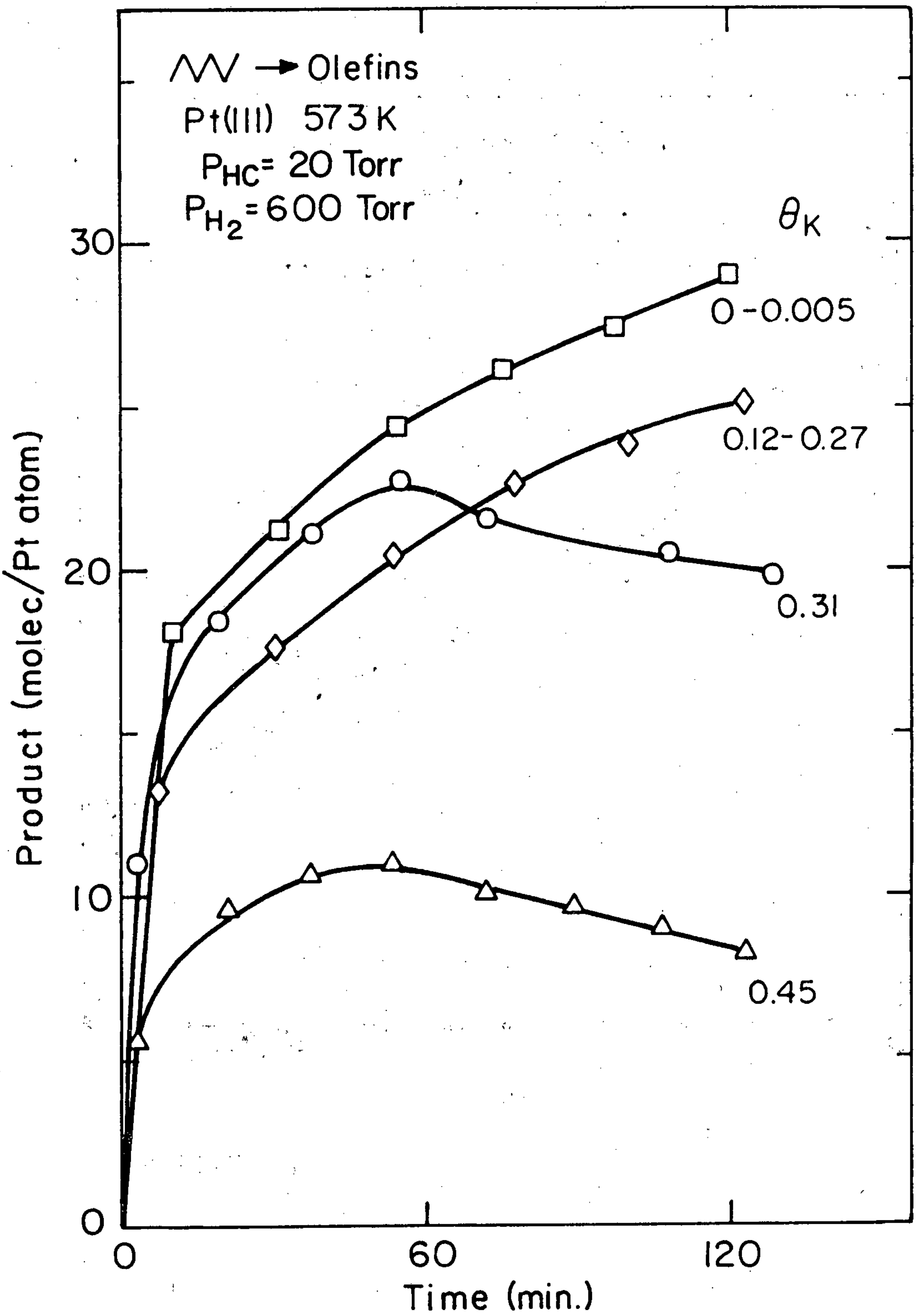

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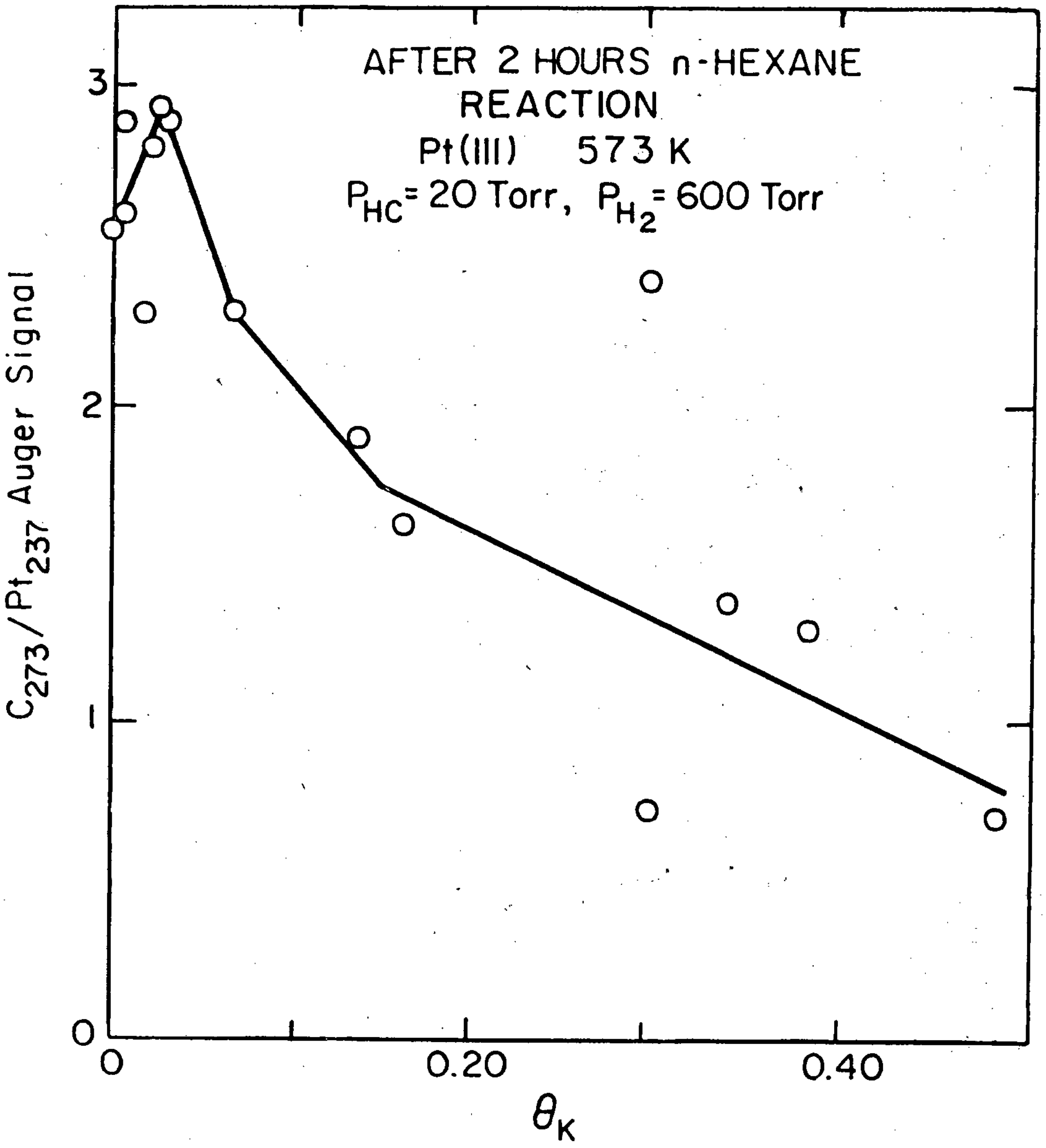
Fig. 5



XBL 823-5293A

Fig. 6

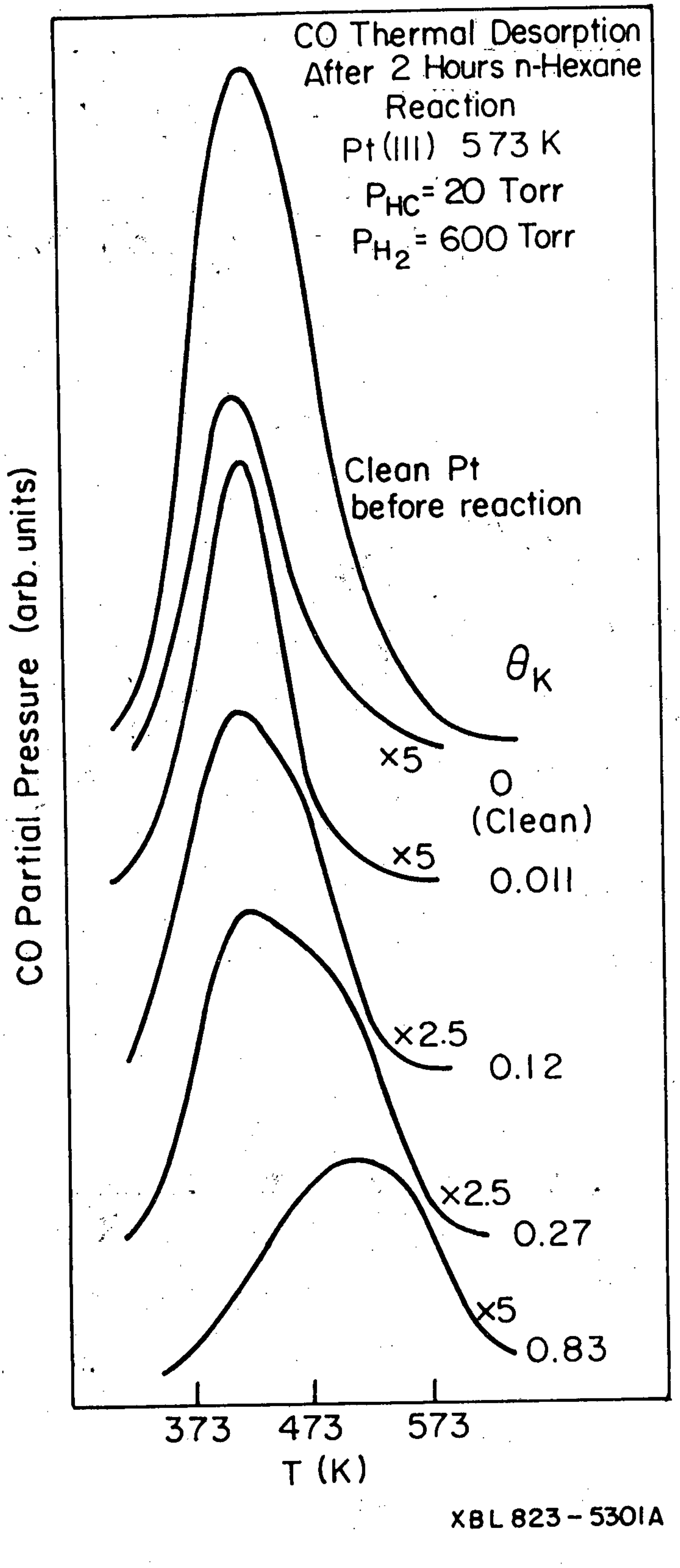
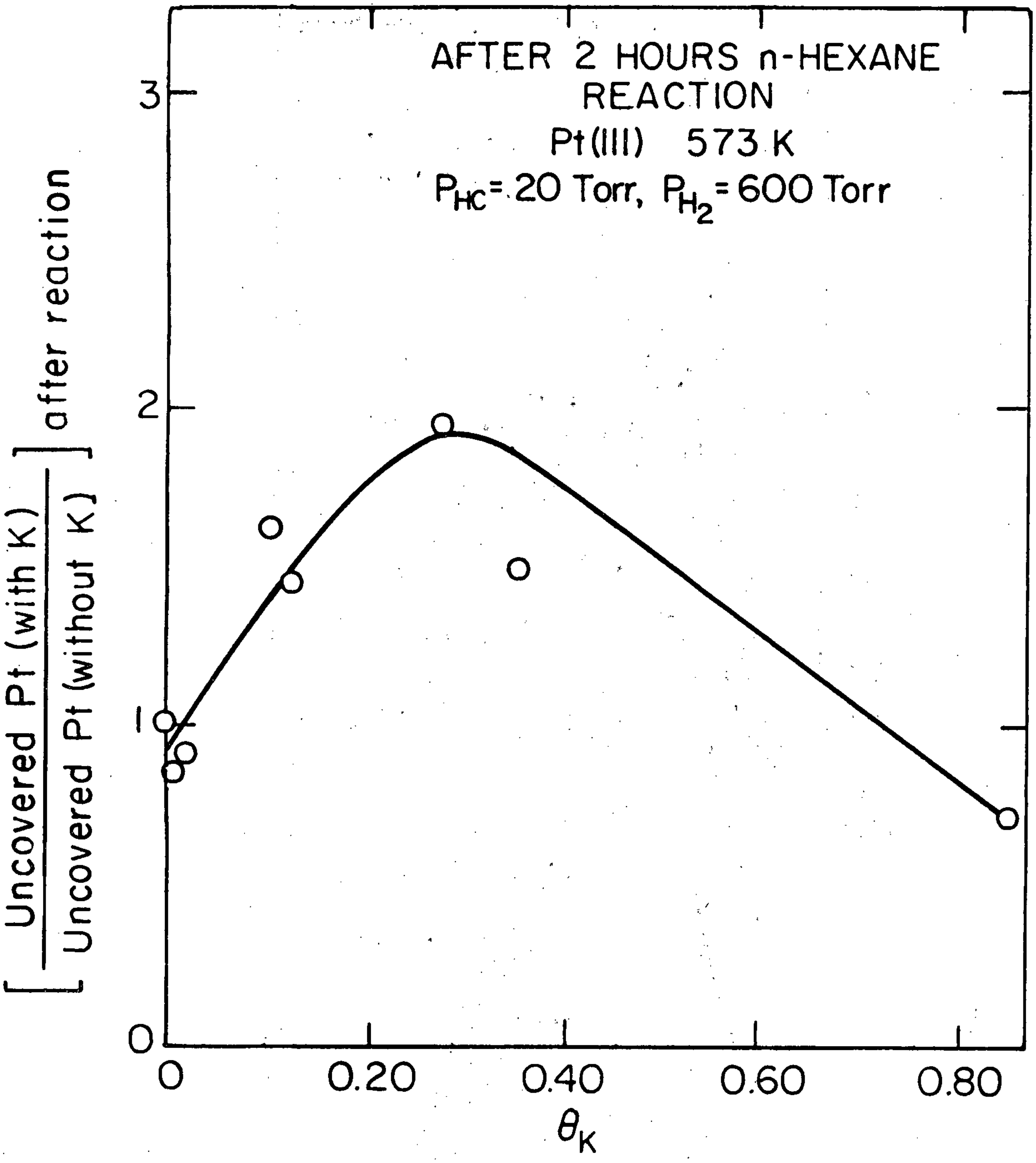
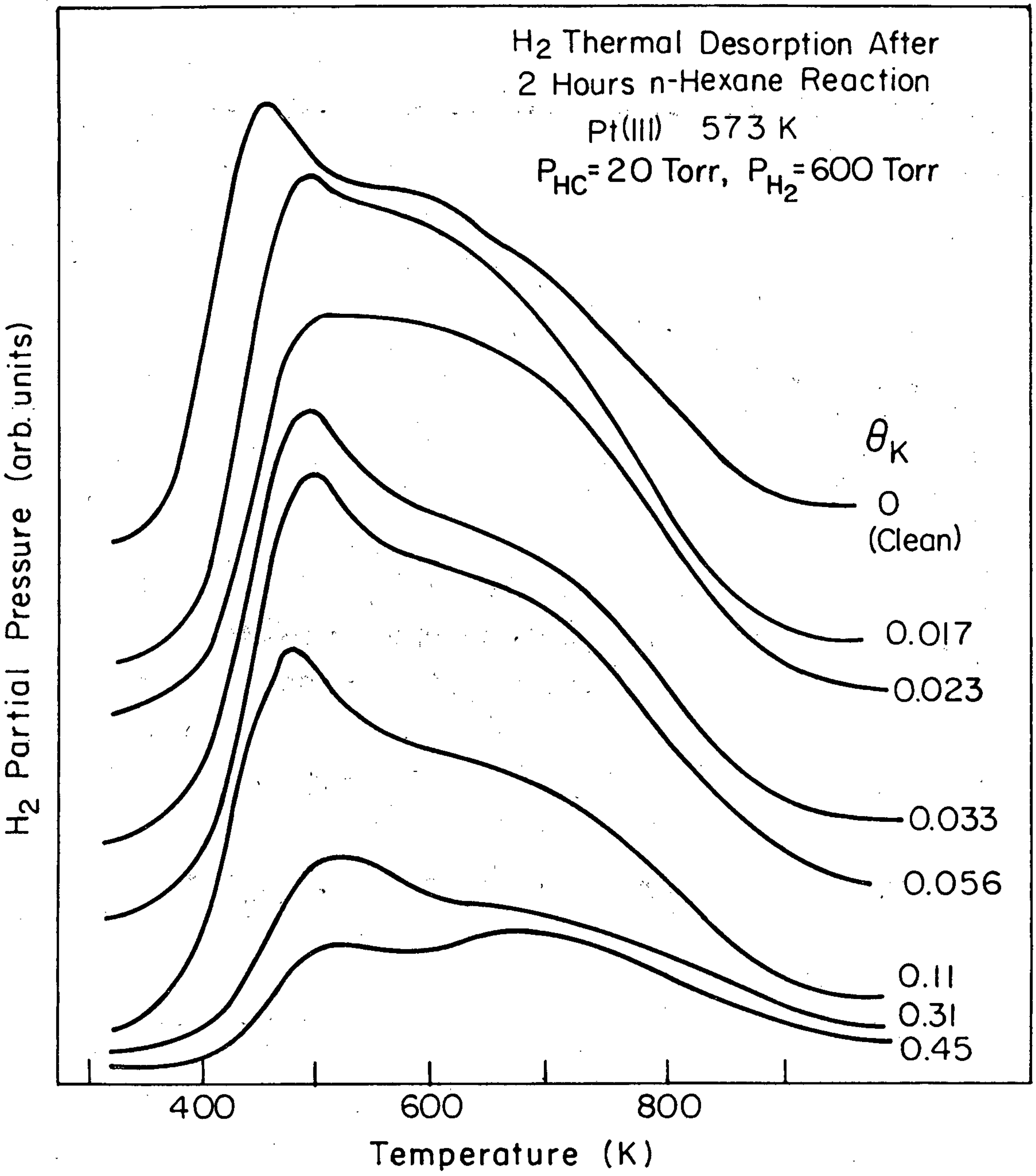

CO Thermal Desorption
After 2 Hours n-Hexane
Reaction
Pt(111) 573 K
P_{HC}= 20 Torr
P_{H_2}= 600 Torr
Clean Pt
before reaction
θ_K
×5
0
(Clean)
×5
0.011
×2.5
0.12
×2.5
0.27
×5
0.83
CO Partial Pressure (arb. units)
373
473
573
T (K)
XBL 823-5301A

Fig. 7



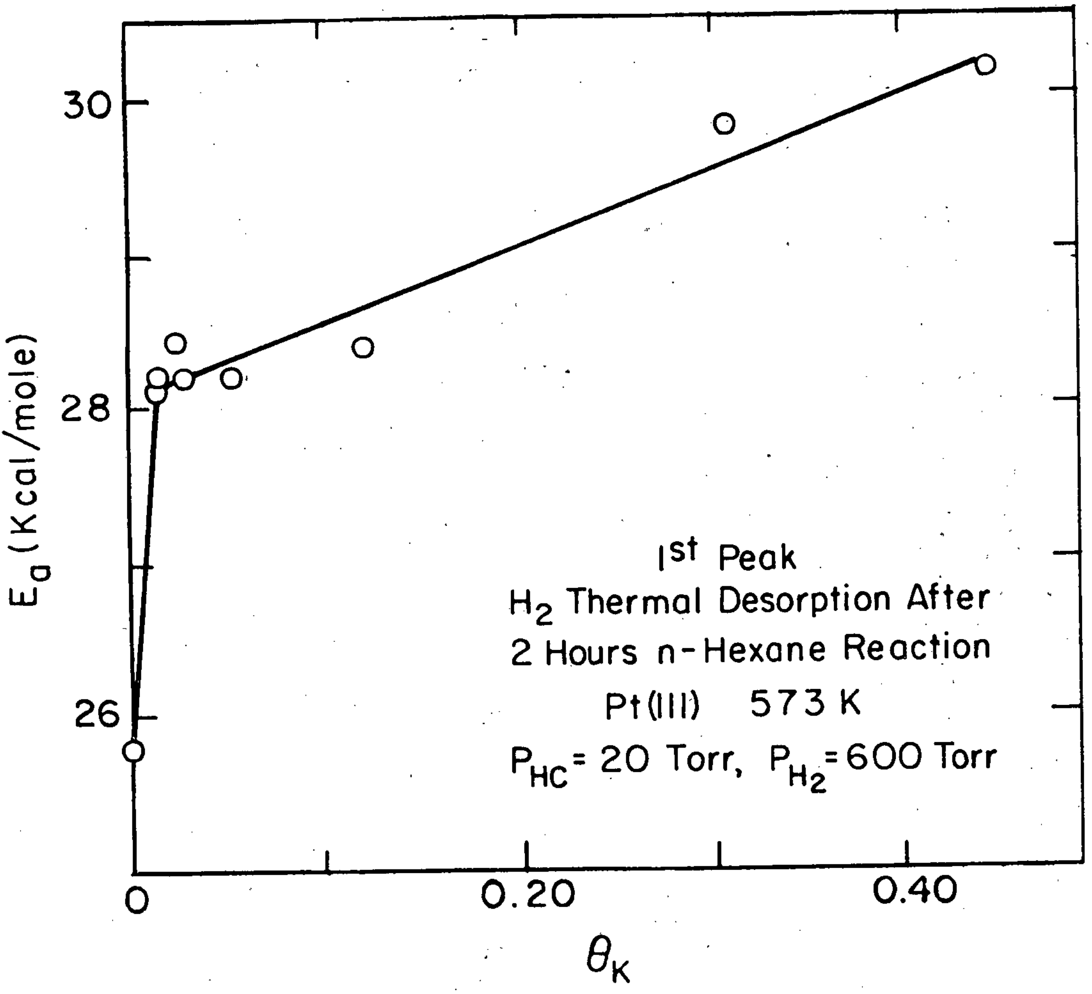
XBL823-5294A

Fig. 8



XBL 823-5303A

Fig. 9



XBL 823-5304 A

Fig. 10

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