

# Lawrence Berkeley National Laboratory

## Lawrence Berkeley National Laboratory

### Title

DEUTERIUM EXCHANGE REACTIONS OF ISOBUTANE, n-HEXANE, AND n-HEPTANE CATALYZED OVER PLATINUM SINGLE CRYSTAL SURFACES

### Permalink

<https://escholarship.org/uc/item/3vd6f1nd>

### Author

Davis, S.M.

### Publication Date

1981-06-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

Submitted to the Journal of Physical Chemistry

DEUTERIUM EXCHANGE REACTIONS OF ISOBUTANE, n-HEXANE,  
AND n-HEPTANE CATALYZED OVER PLATINUM SINGLE  
CRYSTAL SURFACES

S.M. Davis and G.A. Somorjai

June 1981

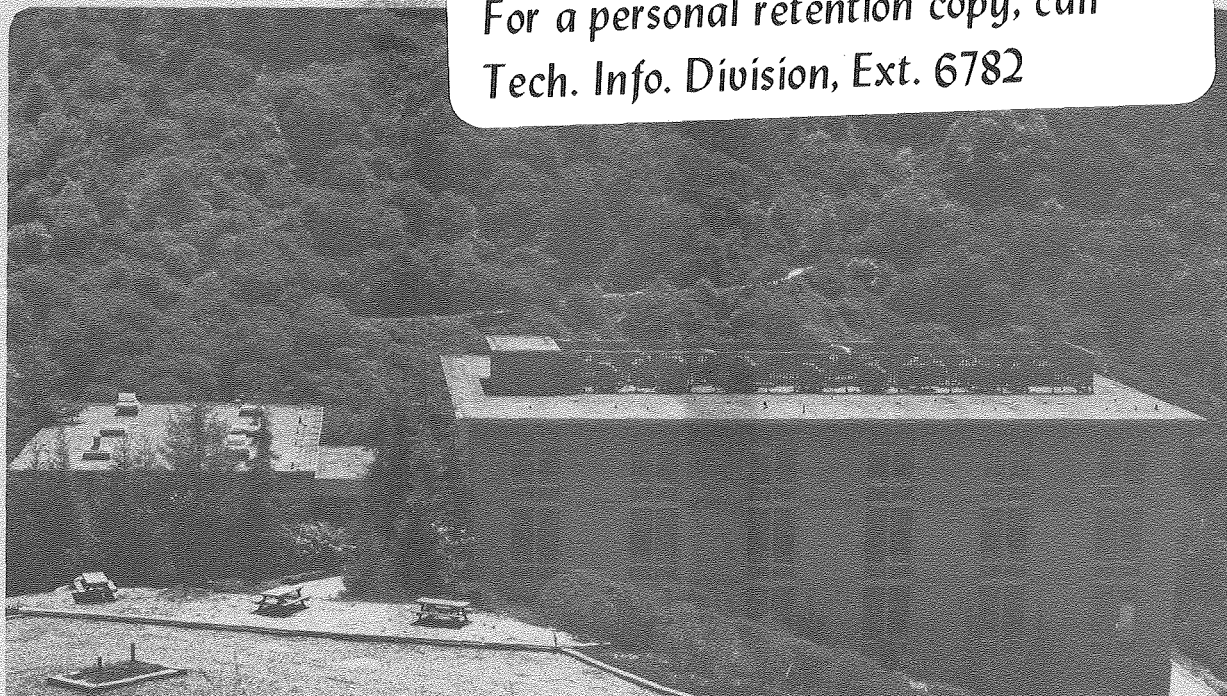
RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

NOV 13 1981

LIBRARY AND  
DOCUMENTS SECTION

**TWO-WEEK LOAN COPY**

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782*



LBL-12149  
c.2

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

DEUTERIUM EXCHANGE REACTIONS OF ISOBUTANE, n-HEXANE, AND n-HEPTANE  
CATALYZED OVER PLATINUM SINGLE CRYSTAL SURFACES

S.M. Davis\* and G.A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley Laboratory  
and  
Department of Chemistry, University of California, Berkeley, CA 94720

Abstract

Isotopic exchange reactions of isobutane, n-heptane, and n-hexane gas have been investigated near atmospheric pressure in the temperature range 500-650 K over the flat (111) and kinked (10,8,7) crystal faces of platinum. The exchange kinetics at low conversion displayed zero activation energy, a first-order dependence on D<sub>2</sub> pressure, and a strong negative order dependence on the surface coverage by strongly bound carbonaceous species. Initial exchange rates and product distributions were not influenced appreciably by the presence of steps and kinks on the platinum surface, and the exchange product distributions varied little with temperature, D<sub>2</sub>-pressure, and surface composition. Hydrocarbon conversion and deuterium exchange rates measured simultaneously for n-hexane reactions catalyzed over Pt(111) revealed that deuterium exchange always occurs more rapidly as compared to all other competing chemical reactions.

\*Permanent address: Exxon Research and Development Laboratories,  
P.O. Box 2226, Baton Rouge, LA 70821

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract W.-7405-ENG-48.

## Introduction

Isotopic exchange reactions catalyzed over platinum between alkanes and deuterium gas have been investigated extensively in order to understand the chemistry of C-H bond breaking processes which accompany dissociative hydrocarbon chemisorption on platinum. Exchange product distributions reported for propane<sup>1</sup>, n-butane<sup>2</sup>, pentanes<sup>1</sup>, hexanes<sup>1</sup>, and heptanes<sup>1</sup> revealed high selectivities for multiple exchange reactions in which several (often all) hydrogen atoms are replaced by deuterium during a single residence on the surface. Notable exceptions occurred only for molecules such as methane<sup>3</sup> and neopentane<sup>4</sup> which contain only primary hydrogen atoms and often display maximum selectivities for exchange of a single hydrogen atom. While the multiplicity of deuterium exchange reactions can often reveal valuable information about the structure and composition of exchange reaction intermediates<sup>5</sup> with few exceptions<sup>2,6</sup>, the exchange reactions have been studied at temperatures that were lower than those required for catalyzed hydrocarbon conversion reactions to occur at measurable rates, and the exchange kinetics were not investigated over a wide range of temperature and deuterium pressure.

The primary purpose of this report is to show that reaction rate studies carried out in deuterium at higher temperatures can be highly revealing if the kinetics of hydrocarbon conversion reactions are studied simultaneously with hydrocarbon-deuterium exchange. This paper describes reaction kinetics and product distributions that were measured for n-hexane, n-heptane, and isobutane deuterium exchange reactions catalyzed over the flat (111) and kinked (10,8,7) platinum single crystal surfaces. The studies were carried out near atmospheric pressure at temperatures between 500 and 650 K. Under these conditions hydrocarbon conversion to hydrogenolysis, isomerization, and cyclization products

occurred simultaneously with deuterium exchange. Substantial inverse deuterium isotope effects that were detected for the hydrocarbon conversion reactions are reported in the following paper.

Several new features of the alkane-D<sub>2</sub> exchange reactions have been identified. Under our reaction conditions deuterium exchange appears to be structure-insensitive, and the kinetics appear to be controlled by the rate of dissociative deuterium chemisorption on the platinum surfaces that are always partially covered by strongly chemisorbed carbonaceous species. The exchange product distributions display little dependence on temperature, D<sub>2</sub> pressure, and surface composition. Under all conditions deuterium exchange occurs more rapidly than hydrocarbon conversion reactions.

### Experimental

Apparatus: All of the deuterium exchange and isotope effect experiments were carried out in an ultrahigh vacuum, high pressure apparatus that was designed for combined surface analysis and catalysis studies using small area (~1 cm<sup>2</sup>) single crystal surfaces<sup>7,8</sup>. This system was equipped with 4-grid electron optics for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), an argon ion gun for crystal cleaning, a quadrupole mass spectrometer for deuterium exchange and thermal desorption studies, and a retractable internal isolation cell which operates as a microbatch reactor in the 10<sup>-2</sup> to 10 atm pressure range. The reaction cell was connected to an external recirculation system (total volume 744 cm<sup>3</sup>) which was fitted with an isolable Wallace & Tiernan gauge, a gas inlet valve, a bellows pump for gas circulation, and a gas chromatograph sampling valve. The recirculation system was interfaced to a small dead volume (ca. 4 cm<sup>3</sup>) connected to a precision leak valve which allowed

samples of the reaction mixture to be withdrawn at 5 to 15 min. intervals and introduced into the main chamber for mass spectral analysis. Each sample withdrawn represented less than 0.7% of the total reaction mixture. Hydrocarbon conversion was monitored with an HP3830 gas chromatograph calibrated with  $\text{CH}_4/\text{N}_2$  mixtures. As flame ionization detector sensitivities for  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$  were identical within 3%, no sensitivity corrections were made for reaction products with variable deuterium content. Using this system, it was possible to measure reaction rates and product distributions for hydrocarbon conversion and hydrocarbon-deuterium exchange all simultaneously.

Materials: The exchange reactions were studied over flat (111) and kinked (10,8,7) platinum single crystal surfaces that were prepared and characterized ( $\pm 1^\circ$ ) in the usual manner<sup>7</sup>. Atomic surface structures for these samples are compared in Figure 1. The (10,8,7) surface has (111) terraces averaging 15.1 Å (about five platinum atoms) in width, separated by monatomic steps with (310) orientation. Both samples were deliberately cut thin (~0.5 mm) so that the polycrystalline edges would contribute no more than 12-16% of the total platinum surface area. The total surface area was used in the calculation of all reaction rates. Research purity isobutane (Matheson, >99.99 mole%), n-hexane (Phillips, >99.96 mole%), n-heptane (Phillips, >99.96 mole%), and deuterium (Matheson, >99.5%  $\text{D}_2$  >99.99%  $\text{H}_2$ , HD,  $\text{D}_2$ ) were used as supplied after outgassing the hydrocarbons by repeated freeze-pumping cycles.

Procedure: The single crystals were cleaned in UHV using a combination of argon ion-sputtering, oxygen pretreatment, and annealing cycles at 1050-1300 K. After the surface composition was characterized by AES, the reaction cell was closed in seconds and pressurized to about 1 atm with  $\text{H}_2$  or  $\text{D}_2$  to cool the sample

below 330 K. After 1 to 2 minutes, the hydrogen was removed, hydrocarbon vapor and deuterium gas were introduced to desired pressures, circulation was commenced, and the crystal was heated to the reaction temperature over a period of about 1 minute. The reaction temperature was continuously regulated to  $\pm 2$  K using a precision temperature controller referenced to a chromel-alumel thermocouple spot-welded to the crystal edge. At the end of the reactions, the samples were cooled to below 320 K, the reaction mixture was removed, the reaction cell was opened, and the Auger spectra were immediately recorded for both crystal faces, all within a period of about 6-9 minutes. Contamination of the surface by impurities such as sulfur and chlorine was never detected (<1-2% monolayer).

Evaluation of the  $D_2$ -exchange data: Exchange rates and product distributions at low conversion (0.3-15%) were calculated from mass spectra that were recorded over the parent ion region at 5-15 minutes intervals. Mass spectra were obtained using 70 eV ionization energy to minimize differences in sensitivity for parent ions with different deuterium content<sup>9</sup>. Most spectra (>80%) were averaged over two consecutive scans with sweep times of 20-30 sec. for each spectrum. Parent peak heights were corrected for carbon-13, statistical cracking to alkyl cations, and production of deuterated alkenes using the procedures described in Appendix I. No corrections were made for isotopic dilution and equal ionization cross sections were assumed for each isomer.

Exchange rates in units of hydrocarbon molecules converted per surface platinum atom per second ( $\text{molec site}^{-1}\text{sec}^{-1}$ ) were estimated graphically from the initial slopes of product accumulation curves measured as a function of reaction time. Since the mass spectrometer sensitivities for deuterated parent ions are lower than those for pure hydrocarbons<sup>9</sup>, the exchange rates determined in



this manner are probably underestimated by 10-30%. The exchange rates were reproducible to within  $\pm 15\%$  and were corrected for background activity by running blank reactions over crystals that were covered by graphitic carbon deposits that formed when the samples were heated to about 800 K in the presence of hydrocarbon. The blank reactions revealed a low level of background exchange activity corresponding to 2-7% of the initial activity measured for clean platinum.

Exchange product distributions were calculated from data that were always collected 12-40 min. after the start of each reaction. The longer times were required at higher reaction temperatures ( $>600$  K) in order to obtain an accurate correction for olefin production (Appendix I). For each calculation the relative concentrations of different isomers,  $d_i\%$ , were determined from corrected parent peak heights where  $d_i\%$  was the percentage of the total reactant hydrocarbon with  $i$  deuterium atoms. The initial product distributions ( $\alpha$ =mole%) were then computed where  $\alpha_i = 10^2 d_i / \sum_{j=1}^n d_j$ , and  $n=10, 14,$  or  $16$  for isobutane,  $n$ -hexane, and  $n$ -heptane, respectively. From these initial distributions, the mean content of deuterium atoms per exchanged molecule,  $\bar{M} = 10^{-2} \sum_{j=1}^n j \alpha_j$ , was evaluated.

## Results

$n$ -Hexane- $D_2$  Exchange Kinetics: Isotopic exchange reactions between  $n$ -hexane and deuterium gas were catalyzed over the flat (111) and kinked (10,8,7) crystal faces of platinum at temperatures between 508 and 658 K with total pressures ranging from 100 to 620 torr. Total product accumulation curves measured as a function of reaction time for Pt(10,8,7) with  $D_2/HC=10$ , and  $P_{tot}=220$  torr are shown at several temperatures in Figure 2. There are two important features: (1) the initial exchange rate was nearly constant over a wide range of temperature, and (2) self-poisoning caused by strongly chemisorbed carbonaceous species became increasingly pronounced with increasing temperature. The same catalytic behavior

was observed for the flat (111) platinum surface. Initial exchange rates measured for both surfaces are compared as a function of temperature in Figure 3. Initial exchange activities were high with turnover frequencies in the range of 2-7 hexane molecules converted per surface platinum atom per second. Close agreement ( $\pm 30\%$ ) was found for the initial rates determined over both surfaces. Also shown in Figure 3 are "steady state" exchange rates measured as a function of temperature after 2-1/2 to 3 hours of reaction. The exchange rates at the longer reaction times decreased markedly with increasing temperature because of the build-up of disordered carbon deposits on the platinum surface, as determined by AES. This is shown clearly in Figure 4 where the steady state rates are plotted as a function of  $(1-\theta_{HC})$ , the fraction of surface not covered by carbonaceous species. Surface coverages by carbonaceous species were estimated from Auger spectra recorded immediately after the reactions using a C<sub>273</sub>/Pt<sub>237</sub> peak-to-peak height ratio of 4.4 as one monolayer. This peak height ratio corresponds to 3.0 (15%) carbon atoms per surface platinum atom<sup>10</sup>. Steady state rates for both surfaces displayed a  $1.6 \pm 0.4$  order dependence on the concentration of vacant platinum sites determined in this manner.

Exchange rates measured for the (10,8,7) platinum surface as a function of D<sub>2</sub> pressure with the temperature held constant at 573 K are shown in Figure 5. The initial exchange rate displayed a first-order ( $1.1 \pm 0.3$ ) dependence on deuterium pressure. The same reaction order for deuterium was obtained when the final rates at the end of the reactions were corrected for surface carbon coverage by dividing by the factor  $(1-\theta_{HC})^{1.6}$ .

n-Hexane-D<sub>2</sub> exchange selectivity: Initial product distributions for n-hexane-D<sub>2</sub> exchange were dominated by a single exchange of one hydrogen atom (C<sub>6</sub>H<sub>13</sub>D), and complete exchange of all 14 hydrogen atoms (C<sub>6</sub>D<sub>14</sub>) under all reaction

conditions. Multiple exchange processes always accounted for 70-85% of the total exchange reaction. Figure 6 shows initial isotopic distributions for Pt(10,8,7) that were determined at several different deuterium pressures with the temperature held constant at 573 K. Exchange product distributions determined as a function of reaction temperature for both platinum surfaces are summarized in Table 1. The kinetic selectivity for complete exchange over single exchange is shown as a function of temperature in the lower half of Figure 7. To compensate for isotopic dilution effects, complete exchange has been represented by the sum  $d_{12}+d_{13}+d_{14}$ . The kinetic selectivity for complete exchange displayed a maximum value of about 3 at temperatures between 550 and 590 K. The average number of deuterium atoms incorporated,  $\bar{M}$ , displayed a similar dependence on reaction temperatures as shown in the upper half of Figure 7. Exchange product distributions determined in "restart" reactions carried out over platinum surfaces already covered with carbonaceous deposits from previous reaction studies were not significantly different from those measured for the initially clean platinum surfaces (Table 1).

Isobutane and n-heptane-D<sub>2</sub> exchange: Results for the exchange of isobutane and n-heptane with deuterium catalyzed over Pt(10,8,7) at 573-623 K are summarized in Table 2. The order of exchange reaction rates at 573 K followed the sequence isobutane > n-hexane n-heptane. Exchange product distributions for isobutane and n-heptane are compared in Table 3. Both reactions were characterized by mostly single or complete exchange with small contributions (1-5%) by all other possible multiple exchange products.

Composition of the carbonaceous deposits: Thermal desorption studies were carried out following the deuterium exchange reactions in order to investigate the composition of the strongly chemisorbed hydrocarbon species which remained

bonded on the platinum surfaces. Deuterium thermal desorption spectra recorded after n-hexane reaction studies over Pt(10,8,7) at 508 and 658 K are shown in Figure 8. The strongly adsorbed species that were deposited during the reactions contained mostly deuterium (>90 %) with very small amounts of residual hydrogen. Sequential dehydrogenation and decomposition of the carbonaceous species took place in two or more steps with broad desorption peak maxima centered at 460 and 640 K.

Comparison between initial reactions rates for n-hexane-D<sub>2</sub> exchange and n-hexane conversion reactions: The total initial rate of n-hexane conversion to form hydrogenolysis, dehydrogenation, cyclization, and isomerization products,  $R_c$ , is compared as a function of temperature with the overall n-hexane-deuterium exchange rate,  $R_x$ , for Pt(111) in Figure 9. The deuterium exchange rates have been corrected for the production of deuterated hexenes and thus refer exclusively to the production of deuterated hexanes (Appendix I). It is clear that deuterium exchange occurred very rapidly compared with hydrocarbon conversion. For the total n-hexane conversion reaction, including dehydrogenation,  $R_d$ , the difference in initial rates,  $R_x/R_c$ , decreased from a factor of 20-30 at 530-500 K to about a factor of 2 at 640 K. Considering only the skeletal rearrangement reactions (isomerization, hydrogenolysis, and cyclization,  $R_{sr}=R_c-R_d$ ), the difference in initial rates,  $R_x/R_{sr}$ , decreased from a factor of 400 at 530 K to about a factor of 10-15 at 640 K. Because all reaction products contained deuterium<sup>7</sup>, the fractional selectivities for hydrocarbon conversion,  $S_c = R_c/(R_c+R_x)$ , and skeletal rearrangement,  $S_{sr} = R_{sr}/(R_c+R_x)$ , could be used to calculate the absolute probabilities that dissociatively chemisorbed molecules will undergo hydrocarbon conversion and skeletal rearrangement, respectively. These absolute reaction probabilities for dissociatively chemisorbed molecules (not be be confused with

the kinetic reaction probability,  $\gamma = (2\pi mkT)^{1/2} R_c / P$  are shown as a function of reaction temperature in Figure 10. The probabilities for skeletal rearrangement and total conversion displayed magnitudes in the range  $10^{-3}$ -0.5 and both increased markedly with increasing reaction temperature.

### Discussion

Structure insensitivity of n-hexane deuterium exchange: The flat (111) and kinked (10,8,7) platinum single crystal surfaces exhibited nearly identical catalytic behavior for isotopic exchange reactions between n-hexane and deuterium gas. Atomic steps and kinks which were present in high concentrations on the (10,8,7,) surface did not produce notable changes in deactivation behavior, exchange product distributions, or exchange catalytic activity. Based on these results, n-hexane-D<sub>2</sub> exchange appears to be a good example of a structure insensitive reaction. Additional studies using (100) and (110) platinum single crystal surfaces would be worthwhile to further confirm this observation.

Deuterium exchange kinetics: The kinetics of deuterium incorporation into both n-hexane and n-heptane catalyzed at 510-650 K displayed an apparent activation energy near zero ( 5 kJ/mole). The rate of n-hexane-D<sub>2</sub> exchange exhibited a first order dependence on D<sub>2</sub> pressure (at 573 K) (Figure 5) and a positive 1.6 order dependence on the apparent concentration of uncovered platinum surface sites (Figure 4). For Pt(10,8,7), the initial and steady state rates could both be expressed by a single rate expression:

$$R_x \approx A(1-O_{HC})^{1.6}(D_2)^{1.1} \quad (1)$$

where A, the apparent pseudo-first order pre-exponential factor, was on the order of  $10^{-20}$  cm<sup>3</sup> Pt atom<sup>-1</sup>sec<sup>-1</sup>. These facts all support a reaction sequence in which the dissociative chemisorption of deuterium molecules at sites containing

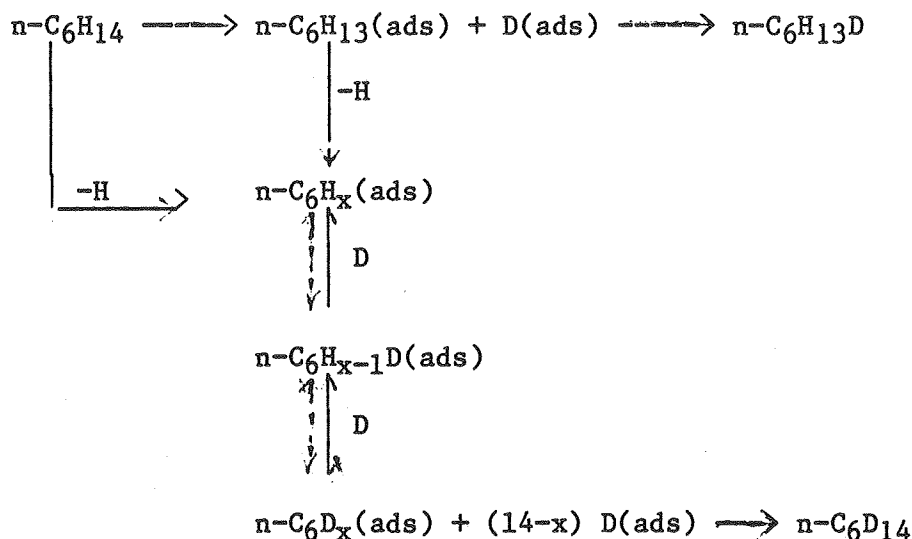
one or, more likely, two uncovered platinum atoms is rate controlling, e.g.



This interpretation is supported by molecular beam reactive scattering studies which revealed that dissociative deuterium chemisorption and  $\text{H}_2\text{-D}_2$  exchange occur over platinum with an activation energy very close to zero<sup>11</sup>. Under our reaction conditions, there appears to exist only a small concentration of free sites located between adsorbed hydrocarbon species where deuterium is chemisorbed at low surface coverage.

Deuterium exchange product distributions: Initial product distributions for n-hexane and n-heptane-deuterium exchange displayed little dependence on temperature,  $\text{D}_2$  pressure, surface structure, and surface composition (Tables 1 and 3, Figure 6). Simple replacement of a single hydrogen atom or complete exchange of all 14 or 16 hydrogen atoms prevailed under all reaction conditions. The selectivity for complete exchange over single exchange increased slowly with increasing temperature until a maximum selectivity was obtained at 560-600 K. Similar behavior was reported by Long et al.<sup>1</sup> for n-hexane- $\text{D}_2$  exchange catalyzed at 340-470 K over platinum films that were prepared in ultrahigh vacuum. Under their reaction conditions ( $\text{D}_2/\text{HC}=9.4$ ,  $P_{\text{tot}}=30$  torr) partial exchange reactions occurred preferentially in methylene groups. Product distributions dominated by complete exchange were also noted by Gault and Kemball for n-hexane- $\text{D}_2$  exchange catalyzed at 330-520 K over palladium and rhodium films<sup>12</sup>.

The series of reaction steps shown below can be used to account for the observed pattern of n-hexane- $\text{D}_2$  exchange selectivity.



Dissociation of a single C-H bond produces surface alkyl species that yield  $n\text{-C}_6\text{H}_{13}\text{D}$  upon deuterium addition. Further dissociation and rearrangement of the surface species yields strongly bonded intermediates which interconvert into  $\text{C}_6\text{D}_x$  species by a series of elementary deuterium addition and hydrogen abstraction processes. These interconversion processes occur rapidly compared with the final deuterium addition step(s) that produce mostly  $n\text{-C}_6\text{D}_{14}$ . While the structures of the intermediate species involved in the interconversion pathway cannot be inferred directly from the exchange product distributions, it is notable that recent studies in our laboratory have shown that ethylidyne ( $\text{Pt}_3\equiv\text{C-CH}_3$ ) species are the most abundant surface intermediates involved in ethylene-deuterium exchange catalyzed over Pt(111) at 350-450 K<sup>13</sup>. Similar alkylidyne and/or alkylidene surface species are expected to be important in the reaction pathway leading to multiple exchange in larger hydrocarbon molecules.

Reaction times, reaction probabilities, and role of adsorbed carbon deposits:

The results reported here clearly demonstrate that hydrocarbon-deuterium exchange reactions take place very rapidly compared with hydrocarbon skeletal rearrangement.

For n-hexane reactions catalyzed over Pt(111) and Pt(10,8,7), the ratio of initial rates  $R_x/R_{SR}$  decreased drastically with increasing temperature from about 400 at 530 K to roughly 10 at 640 K. For isobutane, n-hexane, and n-heptane reactions catalyzed over Pt(10,8,7) at 573 K, the  $R_x/R_{SR}$  ratios varied between 290 (i-C<sub>4</sub>H<sub>10</sub>) and about 50 (n-C<sub>7</sub>H<sub>16</sub>). Because deuterium exchange occurred rapidly compared with all other competing chemical reactions, the overall rates of deuterium exchange can be used to determine minimum surface residence times that are required for dissociative chemisorption and rehydrogenation to occur. Under our reaction conditions, these residence times must be equal to or longer than the reaction times,  $\zeta = (R_x + R_c)^{-1}$ , that were on the order of  $10^{-1}$  sec. Because this time was very long compared with the period between surface collisions of gas phase hydrocarbon molecules ( $\sim 10^{-21}$  sec cm<sup>2</sup>), it is clear that the reaction probability of incident hydrocarbon molecules during a single collision with the platinum surface was very low and that most of the molecules simply desorbed or scattered from the surface without undergoing any chemical reaction. The kinetic reaction probability, calculated directly using the relation  $\gamma = (2\pi mkT)^{1/2} (R_x + R_c) / P_{HC}$  was about  $2 \times 10^{-6}$ .

The strongly chemisorbed carbonaceous species which were deposited on the platinum surfaces during the deuterium exchange reactions were partially dehydrogenerated with an average deuterium (plus hydrogen) content of about 1 atom per surface carbon atom<sup>14</sup>. These species inhibited the dissociative chemisorption of deuterium molecules by site blockage and thereby decreased the rates of the alkane-deuterium exchange reactions. Uncovered platinum sites were required for the exchange reactions to occur at measurable rates. Therefore, it seems clear that the deuterium exchange reactions predominantly take place directly at the metal surface and not by means of hydrogen (or deuterium) transfer reactions with the strongly bound species. This conclusion is supported by carbon-14



radiotracer studies<sup>10,14</sup> which have shown that hydrogen transfer is typically 5-10 times slower than direct hydrogenation using gas phase hydrogen.

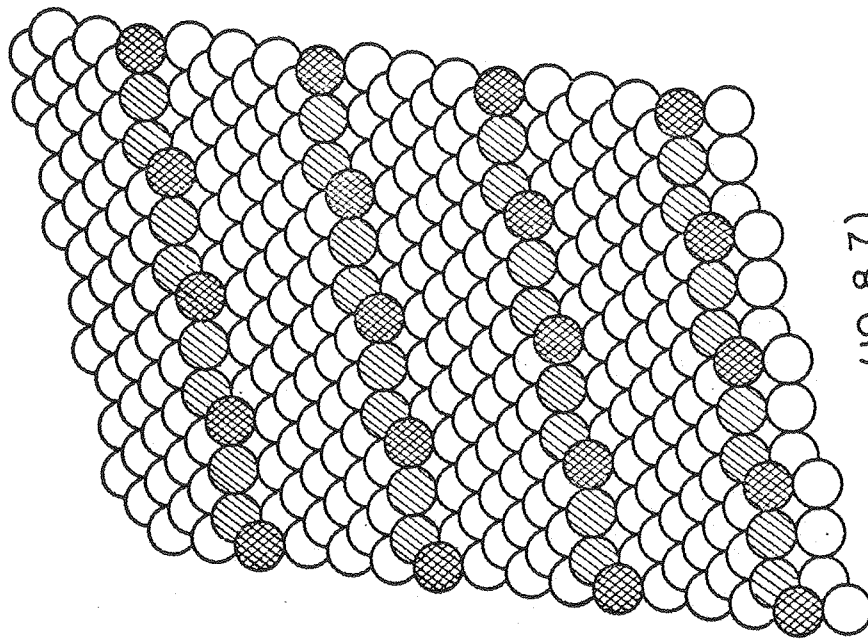
.....

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract W-7405-ENG-48.

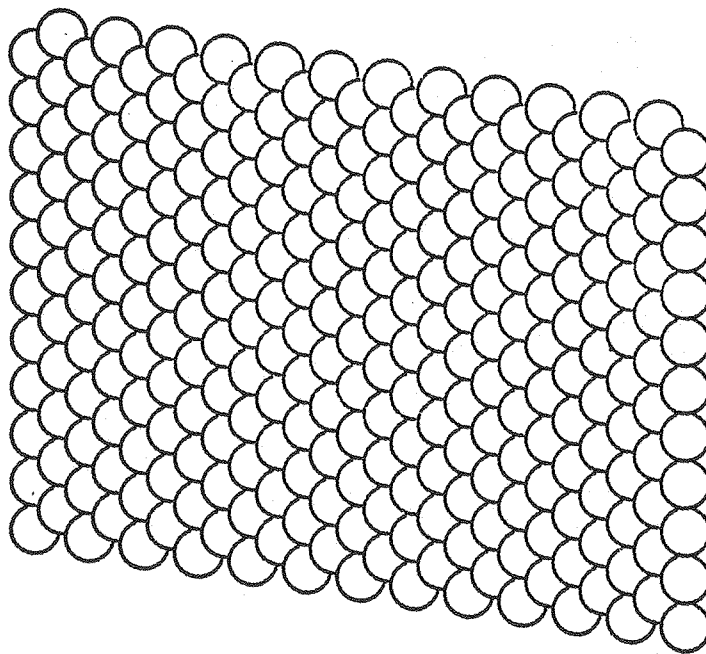
Figure Captions

- Fig.1 Idealized atomic structures for the flat (111) and kinked (10,8,7) platinum single crystal surfaces.
- Fig.2 Total product accumulation curves measured as a function of reaction time for n-hexane-D<sub>2</sub> exchange catalyzed over the kinked (10,8,7) platinum surface.
- Fig.3 Temperature dependence of the initial and steady state rates of n-hexane-D<sub>2</sub> exchange catalyzed over (111) and (10,8,7) platinum single crystal surfaces.
- Fig.4 Correlation of steady state n-hexane-D<sub>2</sub> exchange rates with the fraction of surface not covered by strongly bound carbonaceous species. A C<sub>273</sub>/Pt<sub>237</sub> AES peak-to-peak height ratio of 4.4 was taken as one monolayer corresponding to 3.0 ( $\pm 15\%$ ) carbon atoms per surface platinum atom ( $D_2/HC=10$ ,  $P_{tot}=220$  torr)<sup>10</sup>.
- Fig.5 Dependence of initial and steady state rates on deuterium pressure for n-hexane-D<sub>2</sub> exchange catalyzed over Pt(10,8,7).
- Fig.6 Initial product distributions at several deuterium pressures for n-hexane-D<sub>2</sub> exchange catalyzed over Pt(10,8,7) at 573 K.
- Fig.7 Average number of deuterium atoms incorporated (upper frame) and kinetic selectivities for complete exchange over single exchange (lower frame) determined for n-hexane-D<sub>2</sub> exchange reactions catalyzed at 500-650 K.
- Fig.8 Deuterium thermal desorption spectra recorded after n-hexane-D<sub>2</sub> exchange reactions that were carried out over Pt(10,8,7) at 508 and 658 K. A linear heating rate of  $74 \pm 5$  K sec<sup>-1</sup> was used.
- Fig.9 Comparison between initial reaction rates for n-hexane-D<sub>2</sub> exchange ( $R_x$ ), n-hexane conversion ( $R_c$ ), and n-hexane skeletal rearrangement ( $R_{sr}$ ) reactions catalyzed over Pt(111).
- Fig.10 Absolute reaction probabilities for n-hexane conversion and n-hexane skeletal rearrangement reactions catalyzed over Pt(111) in the presence of deuterium gas.



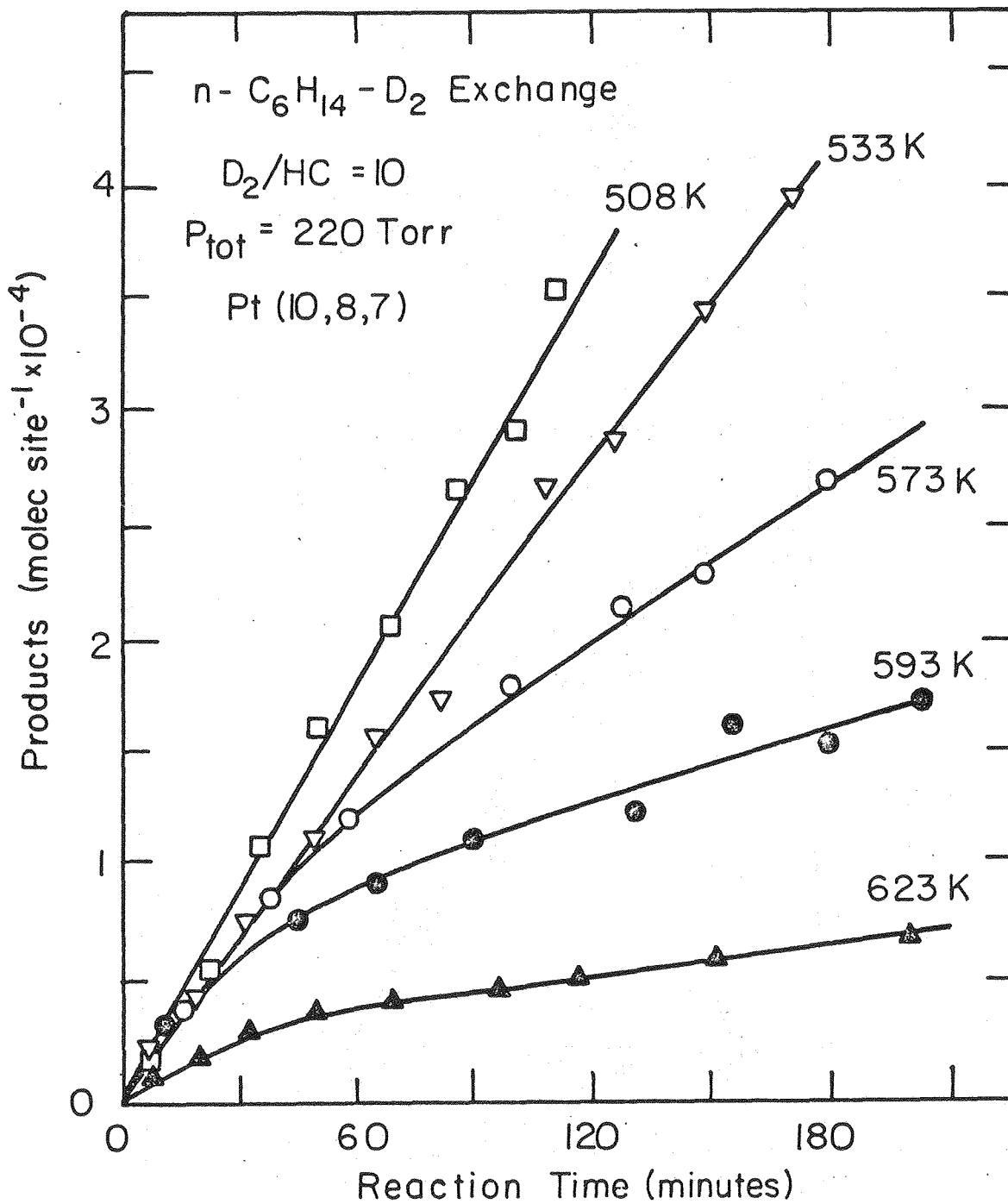
fcc (10, 8, 7)

XBL 8012-12912



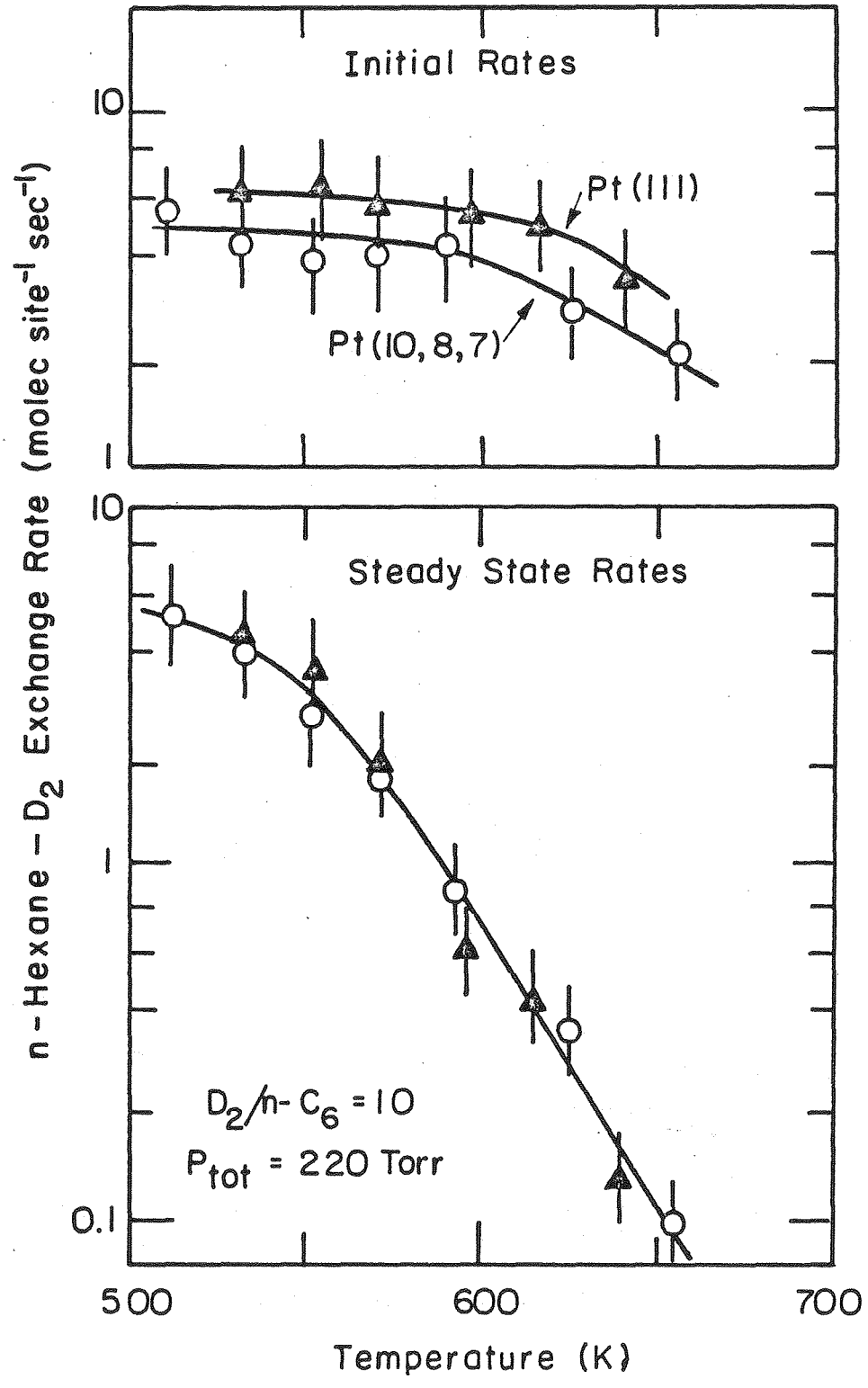
fcc (111)

Fig.1



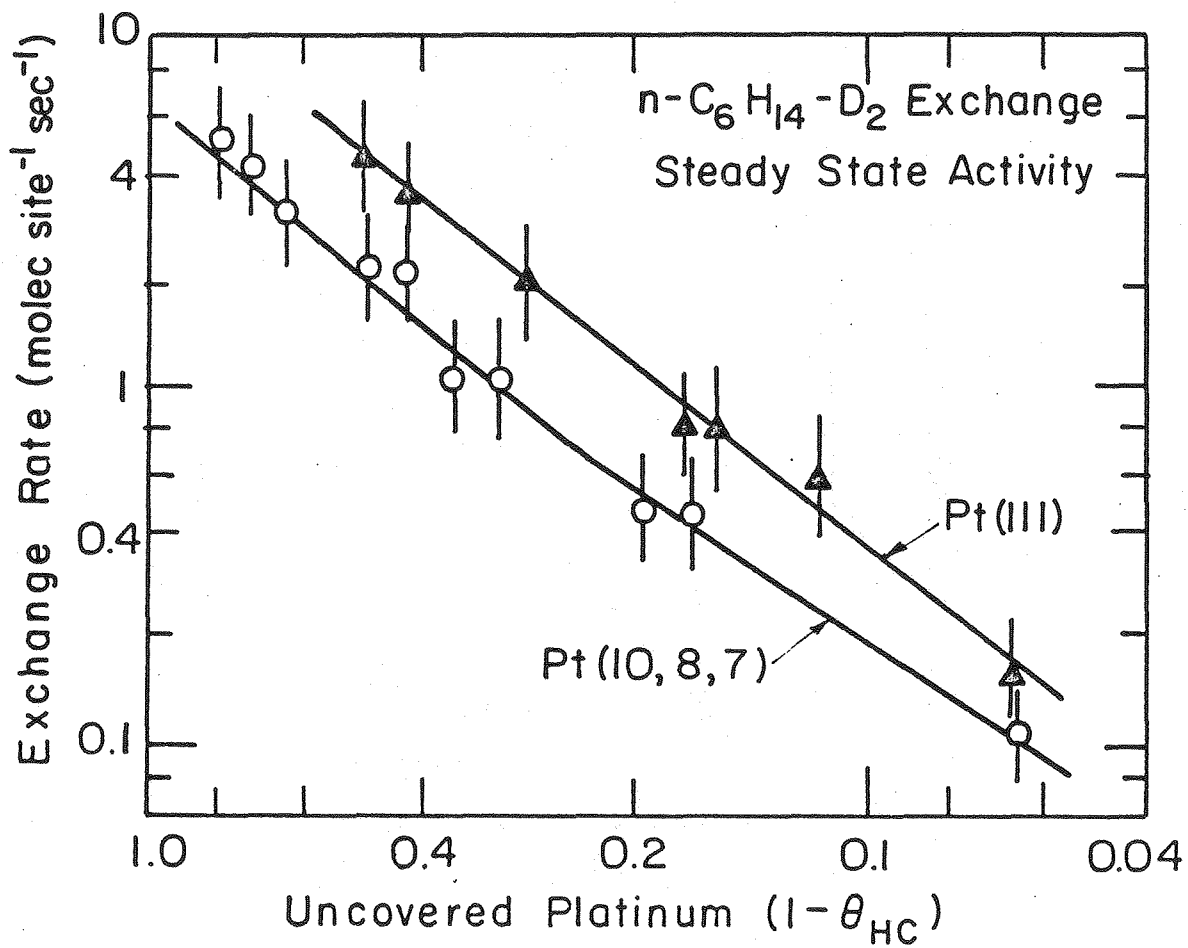
XBL 808-5694

Fig.2



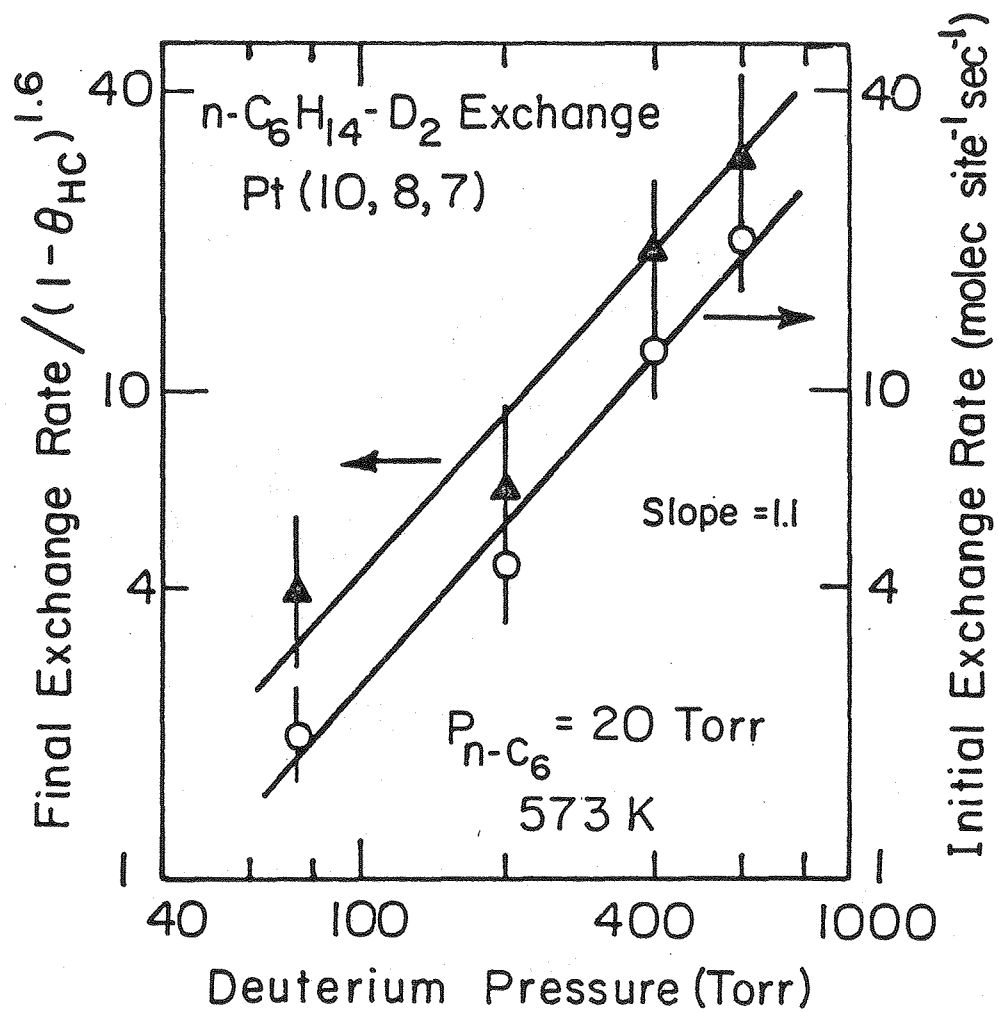
XBL 8010-6079

Fig.3



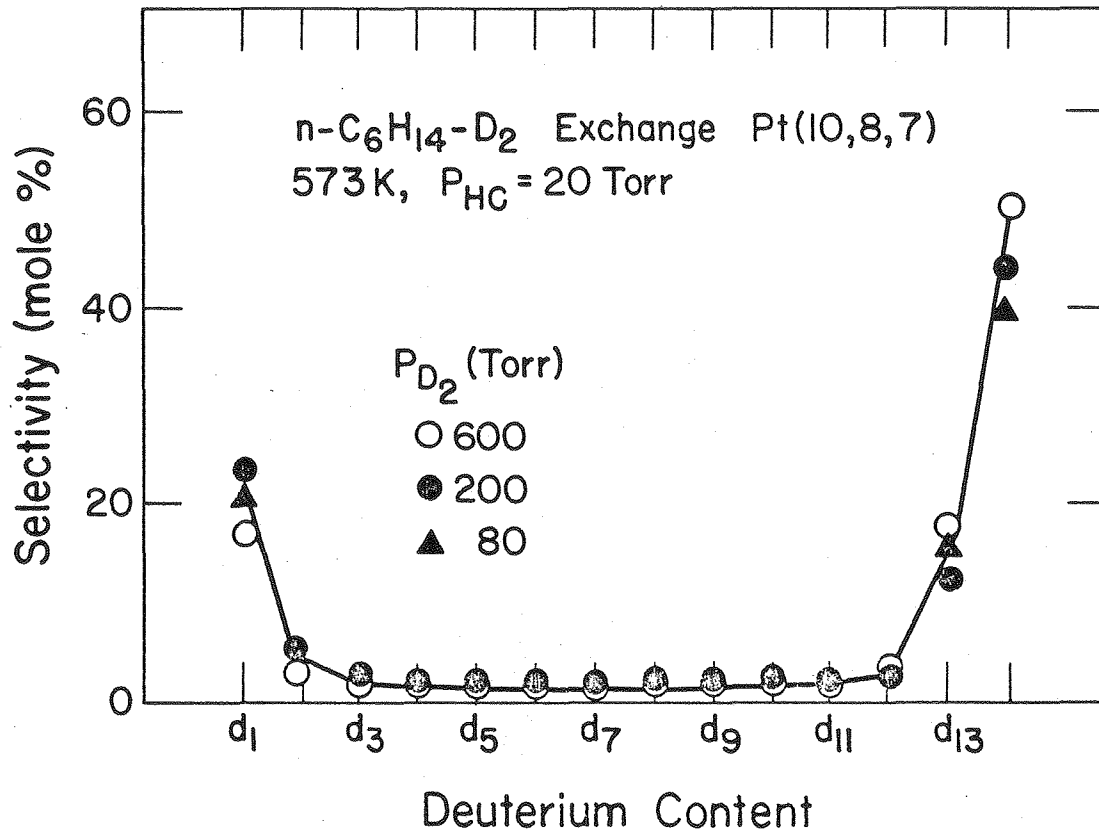
XBL8011-13327

Fig.4



XBL 8011-13328

Fig. 5

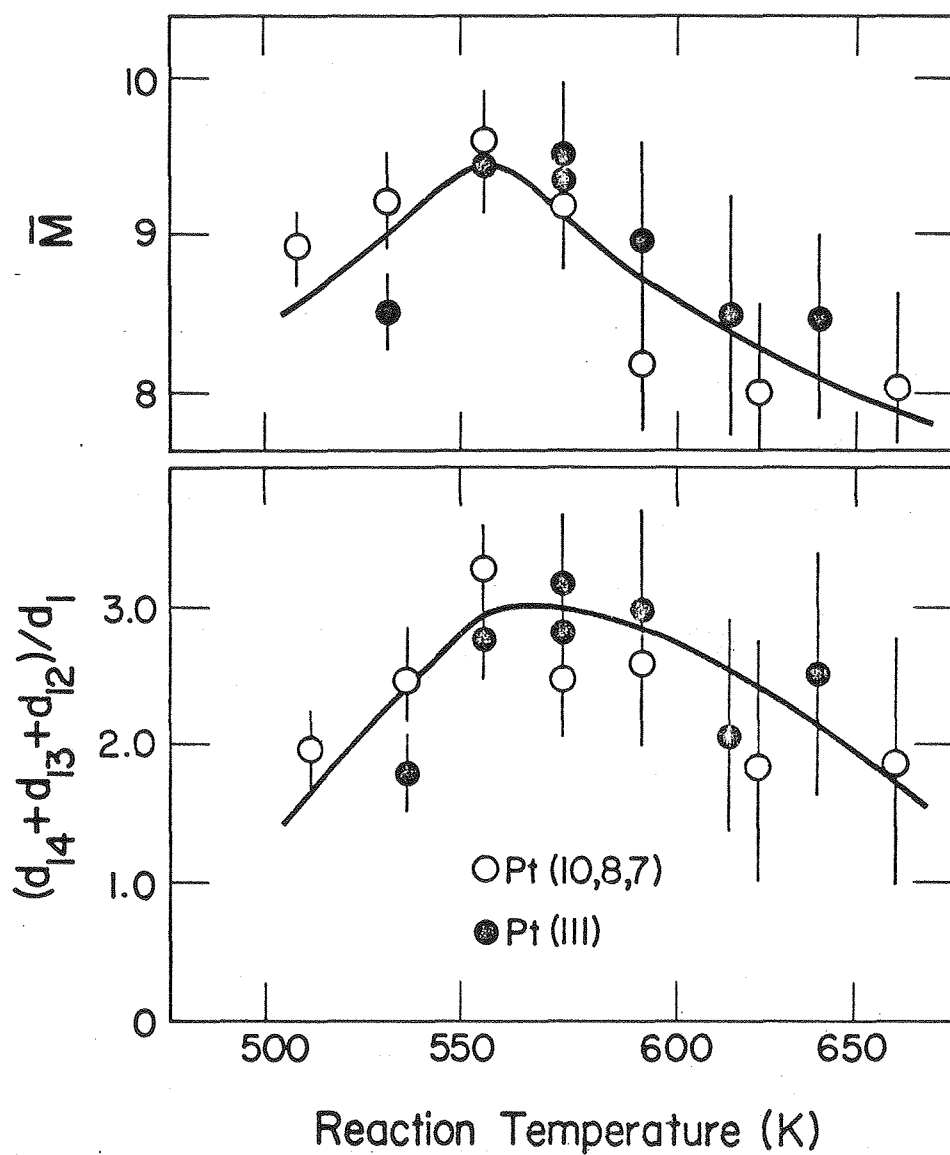


XBL 818-1101

Fig.6

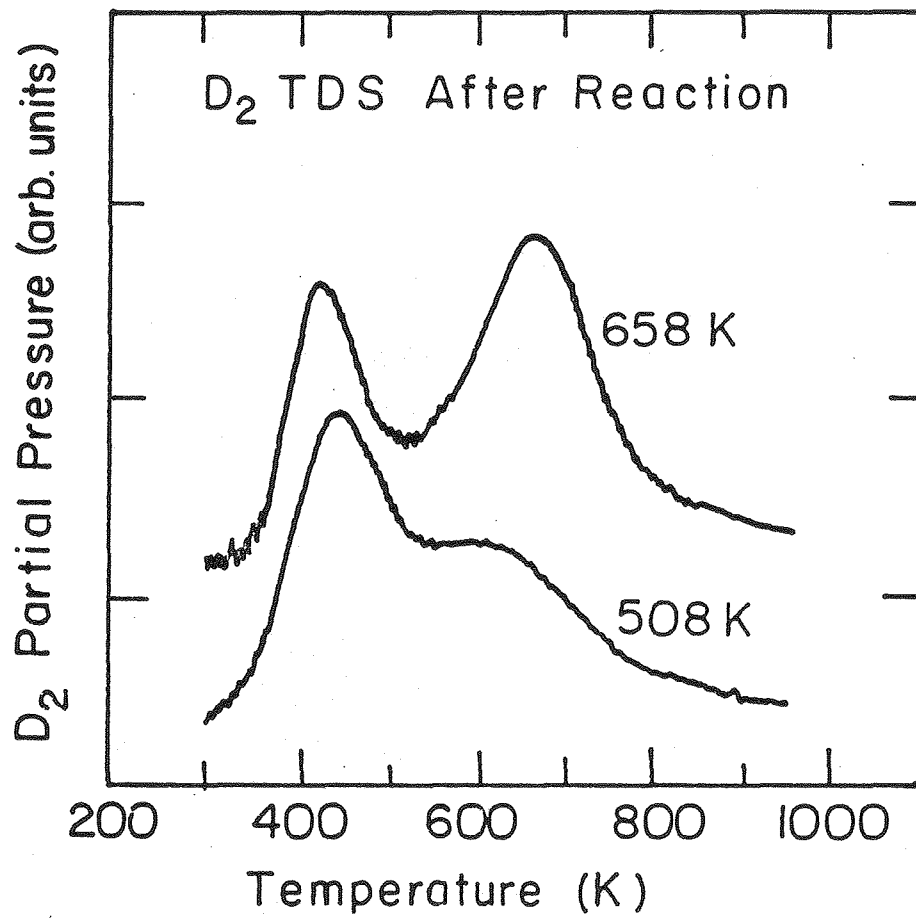


n-C<sub>6</sub>H<sub>14</sub>-D<sub>2</sub> Exchange  
D<sub>2</sub>/HC=10, P<sub>tot</sub>=220Torr



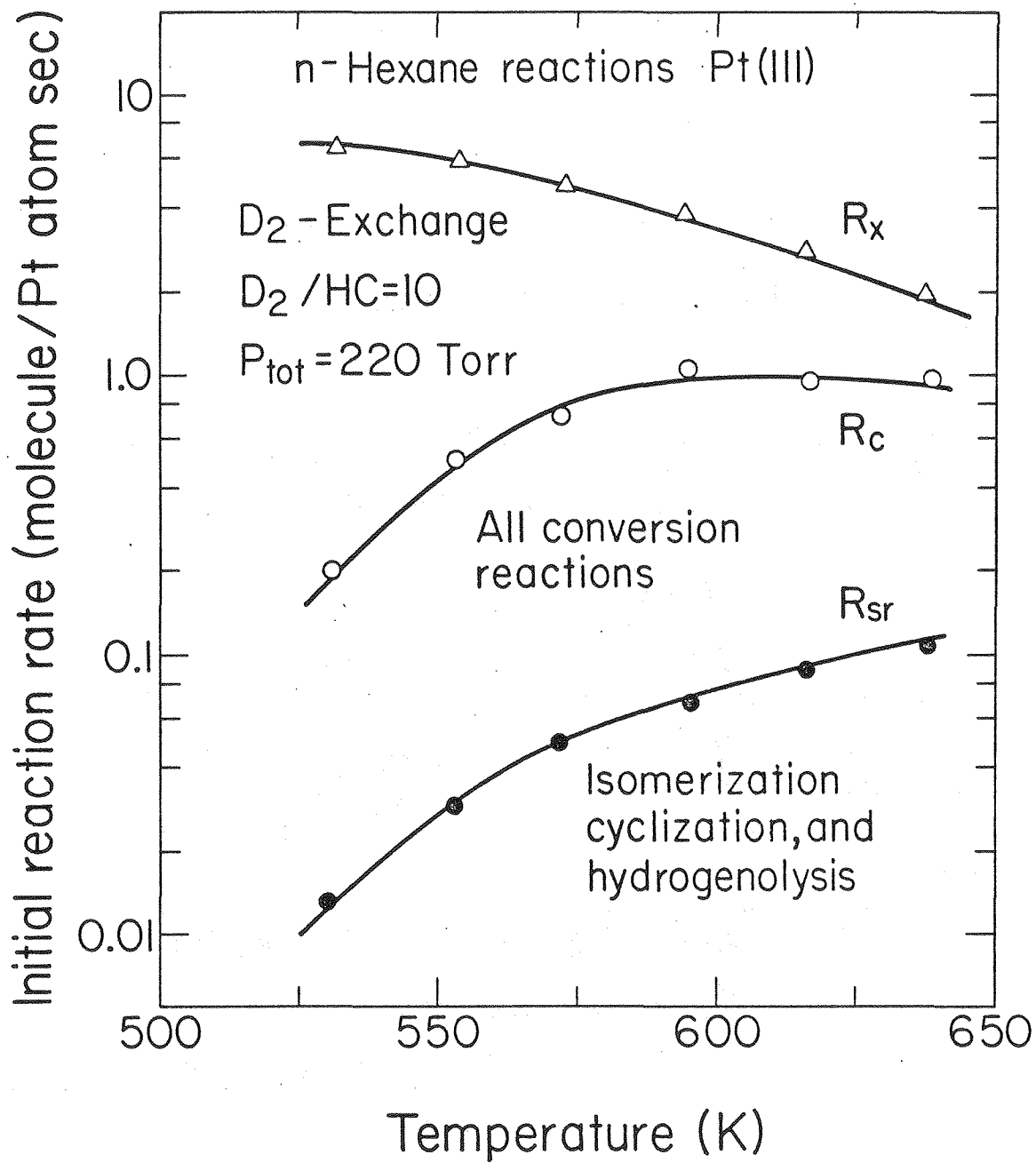
XBL 818-1098

Fig. 7



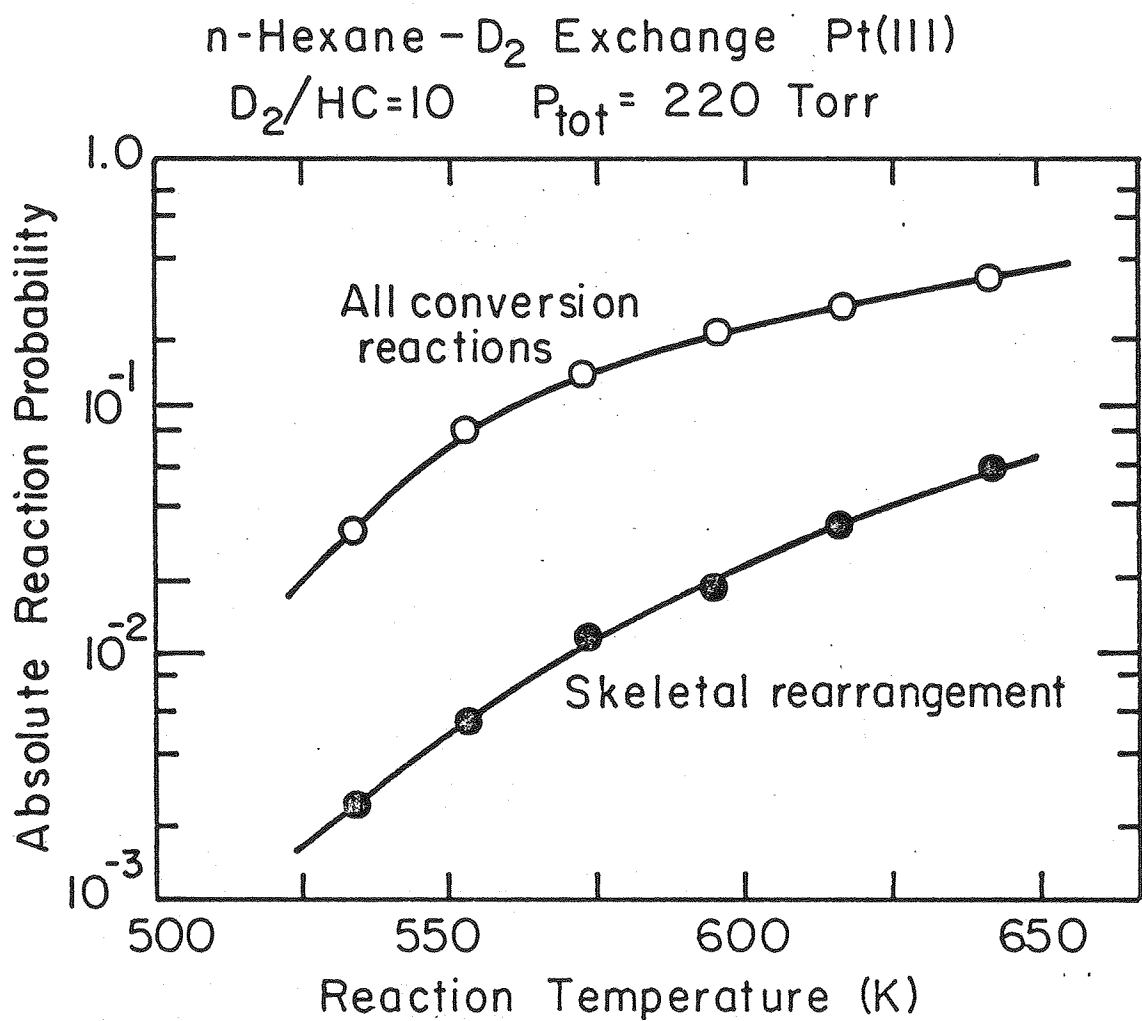
XBL 809-5856

Fig.8



XBL 818-1095

Fig.9



XBL 817-6096

Fig.10

Table 1. Initial Product Distributions for n-Hexane-Deuterium Exchange Catalyzed Over Pt(111) and Pt(10,8,7)<sup>(a)</sup>

Catalyst	T(K)	Initial Distribution (Mole%)													
		d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>5</sub>	d <sub>6</sub>	d <sub>7</sub>	d <sub>8</sub>	d <sub>9</sub>	d <sub>10</sub>	d <sub>11</sub>	d <sub>12</sub>	d <sub>13</sub>	d <sub>14</sub>
Pt(111)	533	27	2.8	2.1	1.6	1.8	1.9	1.8	1.4	1.5	2.8	2.8	3.1	14	33
	553	21	3.1	1.8	2.0	2.1	2.1	2.1	1.5	2.6	3.0	2.2	3.5	15	38
	573	20	4.2	2.7	2.3	2.3	2.5	2.1	0.7	1.0	1.9	3.2	4.4	15	37
	593	17	5.2	3.1	2.9	2.9	3.3	3.2	2.9	2.9	2.9	4.2	4.2	12	34
	638	17	6.2	3.6	3.5	3.6	3.7	3.7	3.5	3.5	3.5	4.1	4.3	11	29
Pt(10,8,7)	508	25	4.5	3.2	1.6	1.5	1.3	1.2	1.3	1.5	2.1	2.5	3.2	14	36
	533	23	3.8	2.7	1.7	1.6	1.6	1.3	1.3	1.6	1.6	2.1	2.6	14	41
	573	24	5.3	1.5	1.4	1.3	1.5	1.5	1.4	1.6	1.6	2.0	2.3	12	43
	593	17	8.1	6.0	2.9	3.1	2.9	3.1	2.9	2.9	2.9	3.2	3.5	10	29
	623	23	5.7	2.3	2.2	2.4	2.4	2.2	2.3	2.3	2.3	1.9	1.9	9	35
	658	23	8.2	3.1	3.0	3.3	3.4	3.1	3.0	3.0	3.0	2.1	2.9	7	32
	573 <sup>b</sup>	14	3.4	3.0	2.5	2.5	2.6	3.0	3.4	3.5	3.5	3.8	4.2	10	39
	623 <sup>b</sup>	22	4.8	2.8	2.3	2.2	2.2	2.2	2.4	2.9	2.9	3.2	4.0	8	38

a) D<sub>2</sub>/HC = 10, P<sub>tot</sub> = 220 Torr

b) Restart experiment over carbon covered platinum

Table 2. Reaction Rates, Average Number of Deuterium Atoms Incorporated, and Surface Carbon Coverages Measured for Isobutane and n-Heptane Deuterium Exchange Catalyzed Over Pt(10,8,7) [a]

Temperature (K)	Exchange Rates Initial	Molec/Pt atom sec) at 120 min.	$\bar{M}$	Cs/Pt [b] (±15%)
isobutane				
573	27	11	8.0	0.7
n-heptane				
573	3.5	1.3	10.0	2.2
591	3.0	0.7	9.6	2.8
623	1.4	0.2	8.9	3.4

[a]  $D_2/HC = 10$ ,  $P_{tot} = 220$  torr.

[b] Carbon atoms per surface platinum atom.

Table 3. Product Distributions for Isobutane and n-Heptane Deuterium Exchange Catalyzed Over Pt(10,8,7)<sup>a</sup>

Reactant	T(K)	Initial Distribution (Mole %)															
		d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>5</sub>	d <sub>6</sub>	d <sub>7</sub>	d <sub>8</sub>	d <sub>9</sub>	d <sub>10</sub>	d <sub>11</sub>	d <sub>12</sub>	d <sub>13</sub>	d <sub>14</sub>	d <sub>15</sub>	d <sub>16</sub>
i-C <sub>4</sub> H <sub>10</sub>	573	12	2.2	1.5	3.4	1.2	3.3	0.7	1.0	22	53	—	—	—	—	—	—
n-C <sub>7</sub> H <sub>16</sub>	573	27	3.7	2.6	1.3	1.1	1.0	0.9	1.0	1.0	1.0	1.0	1.0	2.1	3.7	14	35
	673	21	9.6	3.5	2.6	2.7	2.8	2.4	3.0	2.6	2.4	2.4	2.6	2.6	2.6	11	25

(a) D<sub>2</sub>/HC = 10, P<sub>tot</sub> = 220 torr.

Appendix I

Two levels of calculations were carried out to correct parent peak heights,  $\phi_i$ , measured directly from the mass spectra for (1) olefin production, and (2) carbon-13 and statistical cracking to alkyl cations. While the latter corrections were always small, the olefin corrections became very important for reaction temperatures above about 550 K. Over the temperature range 550-650 K, olefins accounted for 4-34 % of the total uncorrected peak heights initially measured for deuterium containing products.

The total conversion to olefins,  $\gamma$ , was measured as a function of reaction time using the gas chromatograph. With n-hexane (n-heptane), it was assumed that the only olefins produced were  $C_6H_2D_{10}$ ,  $C_6HD_{11}$ , and  $C_6D_{12}$  ( $C_7H_2D_{12}$ ,  $C_7HD_{13}$ , and  $C_7D_{14}$ ). This assumption was consistent with the retention time shifts in the gas chromatograms described in the following paper and the isotopic dilution pattern that was displayed at 94-96 amu (110-112 amu). Hexane parent peak heights at 94-96 amu were corrected for hexenes using

$$(\phi'_{94} + \phi'_{95} + \phi'_{96})/\phi_{86} = (\phi_{94} + \phi_{95} + \phi_{96})/\phi_{86} - \eta\gamma \quad (A1)$$

where the primes indicate corrected peak heights and  $\eta$  was the relative mass spectrometer sensitivity for detecting hexenes and n-hexane. A weighted average for this parameter,  $\eta = 2.45$  was calculated for the temperature range 550-640 K by using API sensitivities tabulated in Table A1 and assuming that hexenes were produced in the equilibrium ratios trans-2-hex/cis-2-hex/trans-3-hex/cis-3-hex/1-hex = 9.3//7.0/4.1/1.6/1.0<sup>15</sup>. The isotopic dilution patterns displayed at 98-100 amu were then employed to estimate the relative heights of the corrected peaks at 94-96 amu using



$$\frac{\phi_{94} - \phi'_{94}}{\phi_{96} - \phi'_{96}} \approx \frac{10}{14} \frac{\phi_{98}}{\phi_{100}} \quad (\text{A2})$$

and

$$\frac{\phi_{95} - \phi'_{96}}{\phi_{96} - \phi'_{96}} \approx \frac{10}{14} \frac{\phi_{99}}{\phi_{100}} \quad (\text{A3})$$

These corrections yielded reasonable (low) values for  $\phi_{94}$ ,  $\phi_{95}$ ,  $\phi_{96}$  under all reaction conditions. At 593-623 K the values tended to become slightly negative as would be expected if small concentrations of olefins with lower deuterium content were produced. Under these conditions, it was assumed that  $\phi_{94} = \phi_{95} = \phi_{96} = \phi_{\min}$  where  $\phi_{\min}$  was the smallest peak height measured for a deuterium containing hexane (usually  $\text{C}_6\text{H}_{10}\text{D}_4$ ). Application of this assumption never introduced more than a 2-8 % error in the initial exchange rate determination.

A series of linear equations was derived for each reactant hydrocarbon in order to correct the alkane peak heights for carbon-13 and statistical cracking to alkyl cations ( $i\text{-C}_4\text{H}_9^+ / i\text{-C}_4\text{H}_{10}^+ = 0.89 = \alpha_4$ ;  $n\text{-C}_6\text{H}_{13}^+ / n\text{-C}_6\text{H}_{14}^+ = 0.055 = \alpha_6$ ;  $n\text{-C}_7\text{H}_{15}^+ / n\text{-C}_7\text{H}_{16}^+ = 0.026 = \alpha_7$ ). For n-hexane, the corrected parent peak heights,  $\theta_i$ , (for  $n\text{-C}_6\text{H}_{14-i}\text{D}_i$ ) were given by

$$\begin{aligned} \theta_{14} &= \phi_{14} - \phi_{13}\beta \\ \theta_{13} &= \phi_{13} - \phi_{12}\beta \\ \theta_{12} &= \phi_{12} - \phi_{11}\beta - \theta_{14}\alpha_6 - 1/14\theta_{13}\alpha_6 \\ \theta_{11} &= \phi_{11} - \phi_{10}\beta - 13/14\theta_{13}\alpha_6 - 2/14\theta_{12}\alpha_6 \\ \theta_j &= \phi_j - \phi_{j-1}\beta - (j+2)/14 \phi_{j+2}\alpha_6 - (13-j)/14 \theta_{j+1}\alpha_6 \quad (j=3-12) \\ &\vdots \\ \theta_2 &= \phi_2 - (\phi_1 - \phi_0)\beta - 4/14\theta_4\alpha_6 - 11/14 \theta_3\alpha_6 - \phi_0\beta' \\ \theta_1 &= \phi_1 - \phi_0\beta - 3/14 \theta_3\alpha_6 - 12/14 \theta_2\alpha_6 \end{aligned} \quad (\text{A4})$$

where  $\beta = 0.0645$  was the experimentally determined correction factor for  $^{13}\text{C}$ ,  $\alpha_6 = 0.055$  was the  $n\text{-C}_6\text{H}_{13}^+ / n\text{-C}_6\text{H}_{14}^+$  peak height ratio, and  $\beta' = 0.00162$  was the

correction factor for two  $^{13}\text{C}$  atoms in unreacted n-hexane. A similar series of equations can be derived easily for n-heptane ( $\beta = 0.042$ ,  $\alpha_4 = 0.89$ ,  $\beta' = 0.001$ ).

To illustrate the use of these correction procedures, Table A2 summarizes a series of example calculations for n-hexane- $\text{D}_2$  exchange catalyzed at 553 K on the (111) platinum surface. The first row lists uncorrected mass spectrometer peak heights,  $\phi_i$ , that were measured at 86 to 100 amu following 29 min. reaction time. In the second row, the 94, 95, and 96 amu peaks have been corrected for the production of deuterated hexenes using  $\gamma = 1.22 \times 10^{-3}$ . The third row summarizes  $\phi_i$  values that are corrected for carbon-13 and statistical cracking to alkyl cations using Eq.A4. The fourth row lists  $d_i$  values, and the fifth row summarizes the initial exchange product distribution (mole %).

.....

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under contract W-7405-ENG-48.

Table A1. Relative mass spectrometer sensitivities for hydrocarbon molecular ions calculated from API Tables [a]

---

C <sub>6</sub> -Hydrocarbon	Parent Ion Sensitivity	C <sub>7</sub> -Hydrocarbon	Parent Ion Sensitivity
n-hexane	1.0	n-heptane	1.0
1-hexene	1.62	1-heptene	1.29
cis-2-hexene	2.25	cis-2-heptene	1.83
trans-2-hexene	2.68	trans-2-heptene	1.89
cis-3-hexene	2.30	cis-3-heptene	1.69
trans-3-hexene	2.64		

---

[a] 70 eV ionization energy.

Table A2. Example calculation of an n-hexane-deuterium exchange product distribution  
 ( $D_2/HC = 10$ ,  $P_{tot} = 220$  torr, 553 K, Pt(111)).

Mass Number (amu)	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
$\phi$ (arb units)	251	17.5	0.71	0.17	0.14	0.15	0.15	0.15	0.17	0.34	0.77	0.21	0.39	0.99	2.60
$\phi'$ (arb units)	251	17.5	0.71	0.17	0.14	0.15	0.15	0.15	0.11	0.19	0.22	0.21	0.39	0.99	2.69
$e$ (arb units)	251	1.4	0.21	0.12	0.13	0.14	0.14	0.14	0.10	0.17	0.20	0.15	0.23	0.97	2.54
$d$ (mole percent)	97.4	0.54	0.081	0.047	0.050	0.054	0.054	0.054	0.039	0.066	0.078	0.058	0.089	0.38	0.99
$\alpha$ (mole percent)	—	21	3.1	1.8	2.0	2.1	2.1	2.1	1.5	2.6	3.0	2.2	3.5	15	38

References

1. M.A. Long, R.B. Moyes, P. B. Wells, and J.L. Garnett, *J. Catal.* 52, 206 (1978).
2. R.S. Dowie, D.A. Whan, and C.Kemball, *J.C.S. Faraday Trans.I*, 68, 2150 (1973).
3. D.W. McKee and F.J. Norton, *J. Catal.* 3, 252 (1964).
4. C. Kemball, *J.C.S. Faraday Trans.* 1, 50, 1344 (1954).
5. V. Ponec, Exchange and Reforming Reactions on Metals and Alloys, in The Chemical  
D.P. Woodruff, eds.) Vol. IV, Elsevier, Amsterdam, 1981.
6. A. Sarkany, L. Gucci, and P. Tetenyi, *J. Catal.* 39, 181 (1975).
7. S.M. Davis, Ph.D. Thesis, University of California, Berkeley, 1981.
8. D.W. Blakely, E. Kozak, B.A. Sexton, and G.A. Somorjai, *J. Vac. Sci. Technol.* 13, 1901 (1976).
9. Y. Amenomiya and R.F. Pottie, *Canad. J. Chem.* 46, 1734 (1968); UTI 100C operating manual.
10. S.M. Davis, B.E. Gordon, M. Press, and G.A. Somorjai, *J. Vac. Sci. Technol.* 20, 000 (1981).
11. M. Salmeron, R.J. Gale, and G.A. Somorjai, *J. Chem. Phys.* 70, 2807 (1979), and references therein.
12. F.G. Gault and C. Kemball, *J.C.S. Faraday Trans* 1, 57, 1781 (1961).
13. M. Salmerón and G.A. Somorjai, *J. Phys. Chem.*, in press.
14. S.M. Davis and G.A. Somorjai, submitted to *J. Catal.*
15. D.R. Stull, E.F. Westrum, and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.