

# Deuterium Exchange Reactions of Isobutane, *n*-Hexane, and *n*-Heptane Catalyzed over Platinum Single Crystal Surfaces

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Isotopic exchange reactions of isobutane, *n*-heptane, and *n*-hexane with deuterium 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 (HC) 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.

## 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. Exchange product distributions reported for propane, *n*-butane, pentanes, hexanes, and heptanes<sup>1,2</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 deuterium exchange are studied simultaneously with hydrocarbon conversion reactions. 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.

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 Section

**Apparatus.** All of the deuterium exchange and isotope effect experiments were carried out in an ultrahigh-vacuum (UHV), 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>–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 and 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 5–15-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 CH<sub>4</sub>/N<sub>2</sub> mixtures. As flame ionization detector sensitivities for C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub> were

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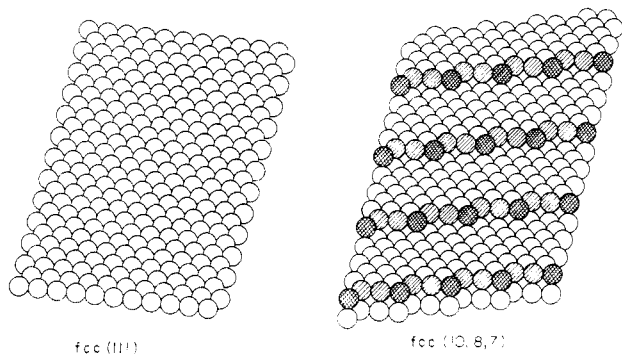
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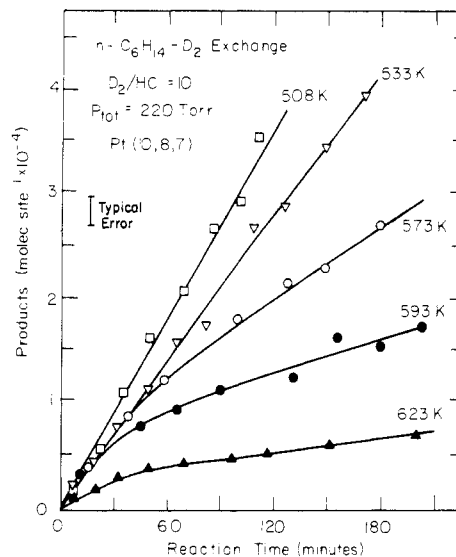
**Figure 1.** Idealized atomic structures for the flat (111) and kinked (10,8,7) platinum single crystal surfaces.

identical within 3%, no sensitivity corrections were made for reaction products with variable deuterium content. With 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 ( $\sim 0.5$  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 mol %), *n*-hexane (Phillips; >99.96 mol %), *n*-heptane (Phillips; >99.96 mol %), and deuterium (Matheson; >99.5%  $D_2$ ; >99.99%  $H_2$ , HD,  $D_2$ ) were used as supplied after outgassing the hydrocarbons by repeated freeze-pumping cycles.

**Procedure.** The single crystals were cleaned under UHV by 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  $H_2$  or  $D_2$  to cool the sample below 330 K. After 1–2 min, 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 min. The reaction temperature was continuously regulated to  $\pm 2$  K with a precision temperature controller 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 min. 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-min intervals. Mass spectra were obtained by 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 s for



**Figure 2.** Total product accumulation curves measured as a function of reaction time for *n*-hexane- $D_2$  exchange catalyzed over the kinked (10,8,7) platinum surface.

each spectrum. Parent peak heights were corrected for carbon-13, statistical cracking to alkyl cations, and production of deuterated alkenes by using the procedures described in the Appendix. No corrections were made for isotropic dilution and equal ionization cross sections were assumed for each isomer.

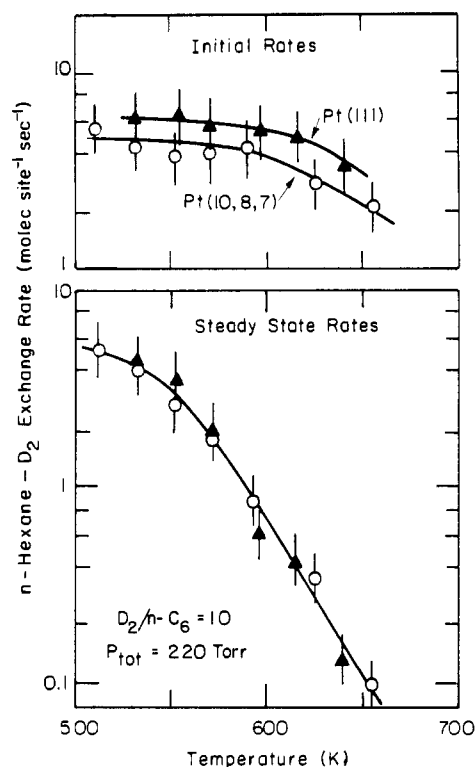
Exchange rates in units of hydrocarbon molecules converted per surface platinum atom per second (molecules  $site^{-1} s^{-1}$ ) were estimated graphically from the initial slopes of product accumulation curves measured as a function of reaction time. Since the mass-spectrometer sensitivities for deuterated 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). 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 ( $\alpha = mol\%$ ) 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,  $M = 10^{-2} \sum_{j=1}^n j \alpha_j$ , was evaluated.

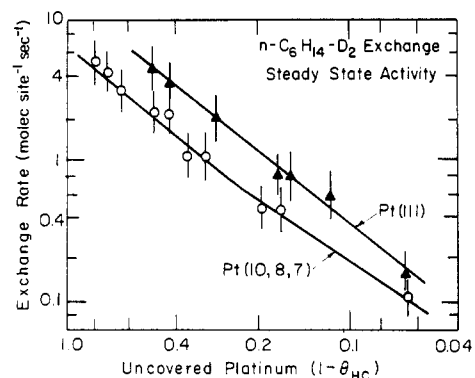
## Results

***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

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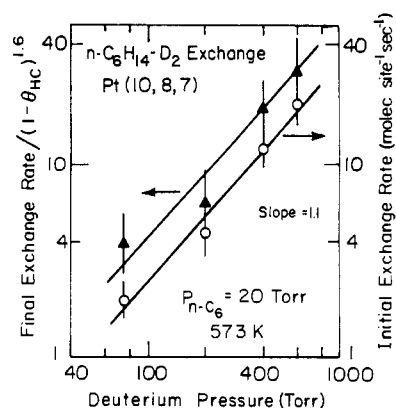


**Figure 3.** Temperature dependence of the initial and steady-state rates of *n*-hexane- $D_2$  exchange catalyzed over (111) and (10,8,7) platinum single crystal surfaces.

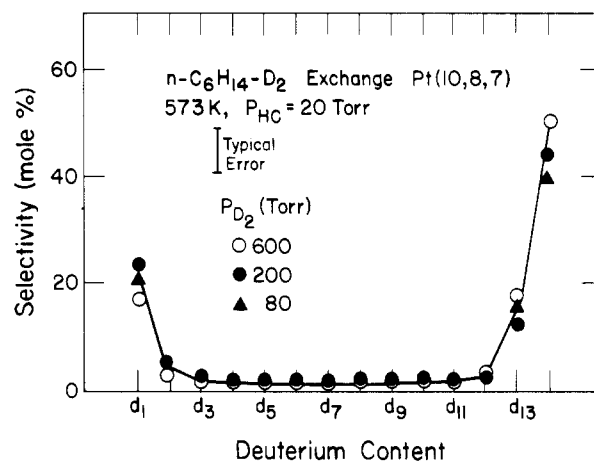


**Figure 4.** Correlation of steady-state *n*-hexane- $D_2$  exchange rates with the fraction of surface not covered by strongly bound carbonaceous species. A  $C_{273}/Pt_{237}$  AES peak-to-peak height ratio of 4.4 was taken as one monolayer corresponding to  $3.0 (\pm 15\%)$  carbon atoms per surface platinum atom ( $D_2/H_C = 10$ ,  $P_{tot} = 220$  torr).<sup>10</sup>

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 2.5–3 h of reaction. The exchange rates at the longer reaction times decreased markedly with increasing temperature because of the buildup of disordered carbon deposits on the platinum surface, as determined by AES. This is shown clearly in



**Figure 5.** Dependence of initial and steady-state rates on deuterium pressure for *n*-hexane- $D_2$  exchange catalyzed over Pt(10,8,7).



**Figure 6.** Initial product distributions at several deuterium pressures for *n*-hexane- $D_2$  exchange catalyzed over Pt(10,8,7) at 573 K.

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 by using a  $C_{273}/Pt_{237}$  peak-to-peak height ratio of 4.4 as one monolayer. This peak height ratio corresponds to  $3.0 (\pm 15\%)$  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  $D_2$  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  $(1 - \theta_{HC})$ .<sup>1,6</sup> Although the influence of hydrocarbon pressure was not studied systematically, one experiment carried out with  $P_{HC} \approx 12$  torr (Pt(10,8,7), 570 K) revealed no significant change in exchange rate or selectivity.

***n*-Hexane- $D_2$  Exchange Selectivity.** Initial product distributions for *n*-hexane- $D_2$  exchange were dominated by a single exchange of one hydrogen atom ( $C_6H_{13}D$ ), and complete exchange of all 14 hydrogen atoms ( $C_6D_{14}$ ) under all reaction conditions. Multiple exchange processes always accounted for 70–85% of the total exchange reaction.

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TABLE I: Initial Product Distributions for *n*-Hexane-Deuterium Exchange Catalyzed over Pt(111) and Pt(10,8,7)<sup>a</sup>

T, K	initial distribution, <sup>b</sup> mol %													
	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>	<i>d</i> <sub>5</sub>	<i>d</i> <sub>6</sub>	<i>d</i> <sub>7</sub>	<i>d</i> <sub>8</sub>	<i>d</i> <sub>9</sub>	<i>d</i> <sub>10</sub>	<i>d</i> <sub>11</sub>	<i>d</i> <sub>12</sub>	<i>d</i> <sub>13</sub>	<i>d</i> <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>c</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>c</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

<sup>a</sup> D<sub>2</sub>/HC = 10, P<sub>tot</sub> = 220 torr. <sup>b</sup> Estimated uncertainties are ±1% for *d*<sub>2</sub>-*d*<sub>12</sub> products, ±4% for *d*<sub>1</sub>, *d*<sub>13</sub> and *d*<sub>14</sub> products. <sup>c</sup> Restart experiment over carbon-covered platinum.

TABLE II: 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)<sup>a</sup>

temp, K	exchange reaction rate, <sup>b</sup> molecules (Pt atom) <sup>-1</sup> s <sup>-1</sup>		$\bar{M}$	Cs/Pt <sup>c</sup>		
	initial	at 120 min				
573	Isobutane		8.0	0.7		
	27	11				
573	<i>n</i> -Heptane		10.0	2.2		
	3.5	1.3				
	591	0.7			9.6	2.8
	623	1.4			0.2	8.9

<sup>a</sup> D<sub>2</sub>/HC = 10, P<sub>tot</sub> = 220 torr. <sup>b</sup> ±20%. <sup>c</sup> Carbon atoms per surface platinum atom (±15%).

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 I. 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*<sub>12</sub> + *d*<sub>13</sub> + *d*<sub>14</sub>. 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

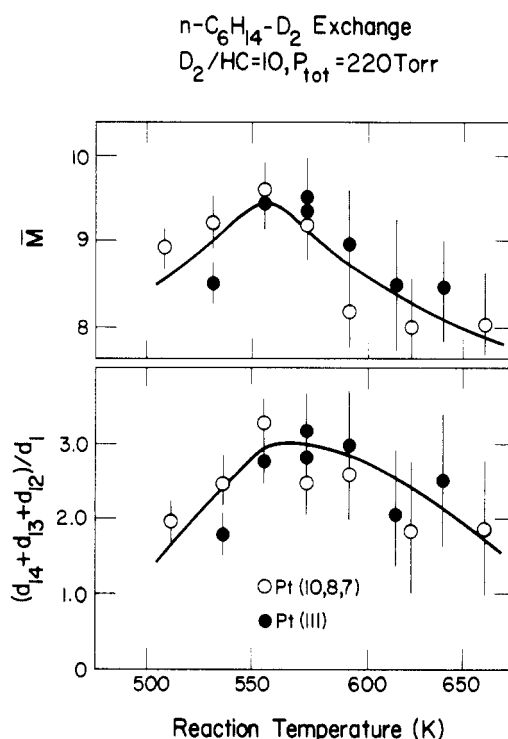


Figure 7. Average number of deuterium atoms incorporated (upper frame) and kinetic selectivities for complete exchange over single exchange (lower frame) determined for *n*-hexane-D<sub>2</sub> exchange reactions catalyzed at 500–650 K.

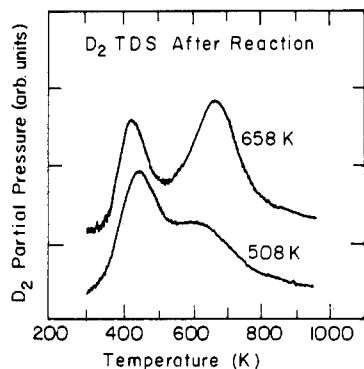
platinum surfaces (Table I).

*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 II. Exchange reaction rates at 573 K decreased with increasing molecular weight in the sequence isobutane >

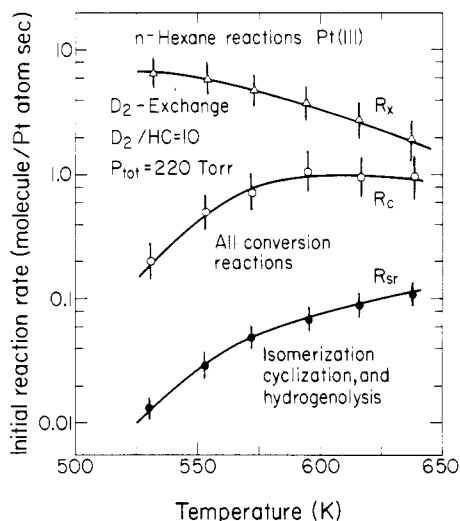
TABLE III: Product Distributions for Isobutane and *n*-Heptane-Deuterium Exchange Catalyzed over Pt(10,8,7)<sup>a</sup>

T, K	initial distribution, <sup>b</sup> mol %															
	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>	<i>d</i> <sub>5</sub>	<i>d</i> <sub>6</sub>	<i>d</i> <sub>7</sub>	<i>d</i> <sub>8</sub>	<i>d</i> <sub>9</sub>	<i>d</i> <sub>10</sub>	<i>d</i> <sub>11</sub>	<i>d</i> <sub>12</sub>	<i>d</i> <sub>13</sub>	<i>d</i> <sub>14</sub>	<i>d</i> <sub>15</sub>	<i>d</i> <sub>16</sub>
573	12	2.2	1.5	3.4	1.2	3.3	0.7	1.0	22	53	<i>i</i> -C <sub>4</sub> H <sub>10</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

<sup>a</sup> D<sub>2</sub>/HC = 10, P<sub>tot</sub> = 220 torr. <sup>b</sup> Estimated uncertainties are ±4% for *d*<sub>1</sub>, *d*<sub>9</sub>, and *d*<sub>10</sub> (isobutane), and *d*<sub>15</sub> and *d*<sub>16</sub> (*n*-heptane) products; all others ±1%.



**Figure 8.** Deuterium thermal desorption spectra recorded after *n*-hexane- $D_2$  exchange reactions that were carried out over Pt(10,8,7) at 508 and 658 K. A linear heating rate of  $74 \pm 5 \text{ s}^{-1}$  was used.

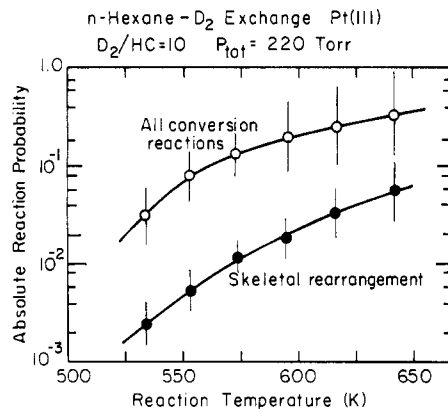


**Figure 9.** Comparison between initial reaction rates for *n*-hexane- $D_2$  exchange ( $R_x$ ), *n*-hexane conversion ( $R_c$ ), and *n*-hexane skeletal rearrangement ( $R_{sr}$ ) reactions catalyzed over Pt(111).

*n*-hexane  $\geq$  *n*-heptane. Exchange product distributions for isobutane and *n*-heptane are compared in Table III. 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) and 508 and 658 K are shown in Figure 8. The strongly adsorbed species that were deposited during the reactions contained mostly deuterium ( $\geq 90\%$ ) 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 Reaction Rates for *n*-Hexane- $D_2$  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). It is clear that deuterium exchange occurred very rapidly compared with hydro-



**Figure 10.** Absolute reaction probabilities for *n*-hexane conversion and *n*-hexane skeletal rearrangement reactions catalyzed over Pt(111) in the presence of deuterium gas.

*carbon 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 530–560 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 to 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.

Within the indicated uncertainties, the overall rates and probabilities for *n*-hexane reactions on the kinked (10,8,7) platinum surface were identical with those shown for Pt(111) in Figures 9 and 10. The surface structure and temperature dependence of the *n*-hexane skeletal rearrangement reactions catalyzed over six different platinum surfaces is reported in detail elsewhere.<sup>11</sup>

## 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. On the basis of these results, *n*-hexane- $D_2$  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 that the deuterium exchange rates display little dependence on the platinum atomic surface structure.

**Deuterium Exchange Kinetics.** The kinetics of deuterium incorporation into both *n*-hexane and *n*-heptane catalyzed at 510–650 K displayed an apparent activation

(11) S. M. Davis, F. Zaera, and G. A. Somorjai, *J. Catal.*, **77**, 439 (1982).

energy near zero ( $\pm 1$  kcal mol<sup>-1</sup>). 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:

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

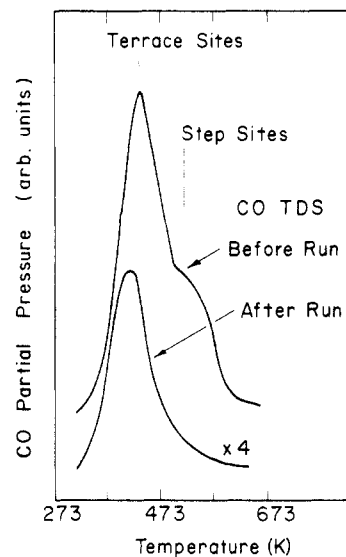
where *A*, the apparent pseudo-first-order preexponential factor, was on the order of 10<sup>-20</sup> cm<sup>3</sup> (Pt atom)<sup>-1</sup> s<sup>-1</sup>. The factor (1 -  $\theta_{\text{HC}}$ )<sup>1.6</sup> reflects the strong dependence of the deuterium exchange rate on the surface coverage by strongly bound carbonaceous deposits as determined by AES. 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 occurs over platinum with an activation energy very close to zero.<sup>12</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.

It should be noted that the dissociative adsorption, sequential dehydrogenation, and rehydrogenation of hydrocarbons chemisorbed on platinum single crystal surfaces is always activated with activation energies of 5–45 kcal mol<sup>-1</sup>.<sup>7,11,13,14</sup> The absence of significant activation energy for the deuterium exchange reaction is consequently best explained if deuterium chemisorption is rate limiting. One alternative explanation for the low activation energy involves intramolecular interconversion of chemisorbed intermediates as in the acetylene-vinylidene rearrangement.<sup>15</sup> Calculations by Simonetta<sup>16</sup> suggest that this rearrangement occurs over Pt(111) with zero activation energy. However, if rearrangement or dehydrogenation were rate limiting, one would not expect a first-order dependence on deuterium pressure.

Reactive scattering studies of the H<sub>2</sub>-D<sub>2</sub> exchange reaction catalyzed at low pressures (10<sup>-6</sup>–10<sup>-3</sup> torr) and 300–1000 K over flat (111) and stepped (332) platinum surfaces indicated that atomic step sites are about 4–7 times more active than terrace sites for dissociative chemisorption of hydrogen and deuterium.<sup>12</sup> Detailed analysis revealed that hydrogen chemisorption was not activated on the stepped surface, whereas a barrier height of 0.5–1.5 kcal mol<sup>-1</sup> was found for H<sub>2</sub> dissociation on the flat surface. This difference in activation energy alone was sufficient to account for the different reaction probabilities of step and terrace sites at low pressures. On the basis of these scattering data, one should expect that, if D<sub>2</sub> chemisorption is rate limiting, the kinked (10,8,7) platinum surface should display higher catalytic activity than Pt-



**Figure 11.** Comparison between CO thermal desorption spectra obtained before and after a *n*-hexane reaction study at 573 K over a stepped (557) platinum single crystal surface. A marked reduction in the concentration of uncovered step sites is apparent following the reaction.

**TABLE IV: Relative Mass-Spectrometer Sensitivities for Hydrocarbon Molecular Ions Calculated from API Tables<sup>a</sup>**

C <sub>6</sub> hydrocarbon	parent ion sensitivity	C <sub>7</sub> hydrocarbon	parent ion sensitivity
<i>n</i> -hexane	1.0	<i>n</i> -heptane	1.0
1-hexene	1.62	1-heptene	1.29
<i>cis</i> -2-hexene	2.25	<i>cis</i> -2-heptene	1.83
<i>trans</i> -2-hexene	2.68	<i>trans</i> -2-heptene	1.89
<i>cis</i> -3-hexene	2.30	<i>cis</i> -3-heptene	1.69
<i>trans</i> -3-hexene	2.64		

<sup>a</sup> 70-eV ionization energy.

(111) for hydrocarbon-deuterium exchange. To rationalize the catalytic behavior observed for the *n*-hexane reaction in the present research, it should be noted that carbon monoxide adsorption-thermal desorption experiments carried out following reaction studies in the presence of excess hydrogen<sup>11</sup> clearly revealed that deposition of carbonaceous deposits derived from *n*-hexane takes place preferentially at atomic step sites; i.e., step sites are preferentially blocked from reactant molecules. This is shown in Figure 11, where CO thermal desorption results are compared before and after reaction on the stepped (557) platinum surface. The relative concentration of uncovered step sites was lowered markedly after this *n*-hexane reaction study at atmospheric pressure and 573 K. Similar behavior was observed for other reactions and other stepped surfaces.<sup>11</sup> Considering the preferential step site blockage, it is not too surprising that the *n*-hexane-D<sub>2</sub> exchange rate was not significantly influenced by the pressure of steps and kinks on the (10,8,7) platinum surface. Since H<sub>2</sub>-D<sub>2</sub> exchange over Pt/SiO<sub>2</sub> catalysts is structure insensitive,<sup>17</sup> it is possible that a change in D<sub>2</sub>-adsorption kinetics with increasing pressure as the surface coverage is increased might also contribute to the absence of structure sensitivity for hydrocarbon-D<sub>2</sub> ex-

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(16) A. Gavezzotti and M. Simonetta, *Surf. Sci.*, **99**, 453 (1980).

(17) O. M. Poltorak and V. S. Boronin, *Russ. J. Phys. Chem. (Engl. Transl.)*, **40**, 1436 (1966); F. J. Kuijers, R. P. Dessing, and W. M. H. Sachtler, *J. Catal.*, **33**, 316 (1974).

(18) F. G. Gault and C. Kamball, *J. Chem. Soc., Faraday Trans. 1*, **57**, 1781 (1961).

TABLE V: Example Calculation of an *n*-Hexane-Deuterium Exchange Product Distribution<sup>a</sup>

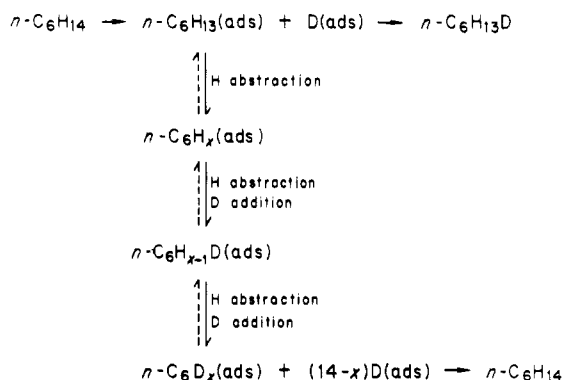
mass no., amu	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
$\phi$ , arb units	251	17.5	0.71	0.17	0.14	0.15	0.15	0.15	0.17	0.34	0.77	0.21	0.39	0.99	2.60
$\phi'$ , arb units	251	17.5	0.71	0.17	0.14	0.15	0.15	0.15	0.11	0.19	0.22	0.21	0.39	0.99	2.69
$\theta$ , arb units	251	1.4	0.21	0.12	0.13	0.14	0.14	0.14	0.10	0.17	0.20	0.15	0.23	0.97	2.54
$d$ , mol %	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
$\alpha$ , mol %	21	3.1	1.8	2.0	2.1	2.1	2.1	2.1	1.5	2.6	3.0	2.2	3.5	15	38

<sup>a</sup>  $D_2/HC = 10$ ,  $P_{tot} = 220$  torr, 553 K, Pt(111).

change at atmospheric pressures.

**Deuterium Exchange Product Distributions.** Initial product distributions for *n*-hexane and *n*-heptane-deuterium exchange displayed little dependence on temperature,  $D_2$  pressure, surface structure, and surface composition (Tables I and III, 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- $D_2$  exchange catalyzed at 340–470 K over platinum films that were prepared under ultrahigh vacuum. Under their reaction conditions ( $D_2/HC = 9.4$ ,  $P_{tot} = 30$  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- $D_2$  exchange catalyzed at 330–520 K over platinum and rhodium films.<sup>12</sup>

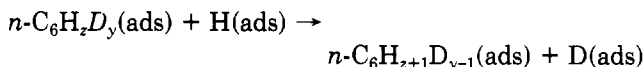
The following series of reaction steps can be used to account for the observed pattern of *n*-hexane- $D_2$  exchange selectivity:



Dissociation of a single C–H bond produces surface alkyl species that yield  $n-C_6H_{13}D$  upon deuterium addition. Further dissociation and rearrangement of the surface species yield strongly bonded intermediates which interconvert into  $C_6D_x$  species by a series of elementary deuterium addition and hydrogen abstraction processes. These interconversion processes must occur rapidly compared with the final deuterium addition step(s) that produce mostly  $n-C_6D_{14}$ . 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 ( $Pt_3\equiv C-CH_3$ ) 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.

For this reaction sequence to account for the observed isotopic distribution, it is assumed that the surface con-

centration of chemisorbed hydrogen is small (e.g.,  $\theta_D \gg \theta_H$ ) so that reactions like



are not important. This assumption is clearly valid as indicated by the absence of significant isotopic dilution in complete exchange products. Using experimental  $d_{13}/d_{14}$  selectivities and neglecting isotope effects for hydrogen or deuterium addition (elimination), one can easily obtain an upper limit for  $\theta_H/\theta_D$  of order 0.01–0.03 from the binomial distribution function.<sup>19</sup>

The maxima in complete exchange selectivity and average number of deuterium atoms incorporated that were detected with increasing reaction temperature (Figure 7) appear to result from competition between reaction pathways for complete exchange and hydrocarbon conversion. As dehydrogenation and skeletal rearrangement become significant relative to simple exchange at temperatures above about 580 K, surface intermediates that would otherwise lead to complete exchange are preferentially converted along the other reaction pathways. Although the deuterium distributions of the hydrocarbon conversion products could not be accurately determined, results discussed in a separate paper<sup>11</sup> clearly indicate that these products were always extensively deuterated, most probably perdeuterated.

**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; i.e., dissociative chemisorption is effectively reversible as compared to the rates of hydrogenolysis, isomerization, and cyclization. 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*- $C_4H_{10}$ ) and about 50 (*n*- $C_7H_{16}$ ). 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  $10^{-1}$  s. Because this time was very long compared with the period between surface collisions of gas-phase hydrocarbon molecules ( $\sim 10^{-21}$  s  $cm^2$ ), 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

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reaction probability, calculated directly from the relation  $\gamma = (2\pi mkT)^{1/2}(R_x + R_c)/P_{HC}$ , was about  $2 \times 10^{-6}$ .

The order of initial alkane-deuterium exchange reaction rates (isobutane > *n*-hexane  $\geq$  *n*-heptane) indicates that the residence time required for dissociation and rehydrogenation to take place increases with increasing molecular weight. These differences in surface residence time appear to result from differences in competition between deuterium and hydrocarbon for uncovered platinum surface sites. Hexane and heptane presumably compete more effectively than isobutane, thereby reducing the steady-state concentration of vacant sites that is available for deuterium chemisorption. Consequently, the deuterium exchange rates are lowered for *n*-hexane and *n*-heptane as compared to isobutane. This interpretation is strongly supported by the detailed studies of Maurel et al.<sup>20</sup> which revealed that equilibrium constants for reversible dissociative alkane chemisorption on platinum increase with increasing molecular weight and decreasing substitution.

The strongly chemisorbed carbonaceous species which were deposited on the platinum surfaces during the deuterium exchange reactions were partially dehydrogenated with an average deuterium (plus hydrogen) content of about one atom per surface carbon atom.<sup>11,14</sup> These species inhibited the dissociative chemisorption of deuterium molecules and thereby decreased the rates of alkane-D<sub>2</sub> exchange. Uncovered sites were required for the exchange reactions to occur at measurable rates.<sup>11</sup> Therefore, it seems clear that the deuterium exchange reactions predominantly take place directly at the metal surface and not by means of hydrogen (deuterium) transfer reactions with the strongly bound species. This conclusion is substantiated by carbon-14 radiotracer studies<sup>10,14</sup> which showed that hydrogen transfer is at least 5–10 times slower than direct hydrogenation using gas-phase hydrogen.

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## Appendix

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 by using the gas chromatograph. With *n*-hexane (*n*-heptane), it was assumed that the only olefins produced were C<sub>6</sub>H<sub>2</sub>D<sub>10</sub>, C<sub>6</sub>HD<sub>11</sub>, and C<sub>6</sub>D<sub>12</sub> (C<sub>7</sub>H<sub>2</sub>D<sub>12</sub>, C<sub>7</sub>HD<sub>13</sub>, and C<sub>7</sub>D<sub>14</sub>). 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 by 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 IV and assuming that hexenes were produced in the equilibrium ratios *trans*-2-hex/*cis*-2-hex/*trans*-3-hex/*cis*-3-hex/1-hex = 9.3/7.04/4.1/1.6/1.0.<sup>21</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 by using

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

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

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 C<sub>6</sub>H<sub>10</sub>D<sub>4</sub>). 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*-C<sub>4</sub>H<sub>9</sub><sup>+</sup>/*i*-C<sub>4</sub>H<sub>10</sub><sup>+</sup> = 0.89 =  $\alpha_4$ ; *n*-C<sub>6</sub>H<sub>13</sub><sup>+</sup>/*n*-C<sub>6</sub>H<sub>14</sub><sup>+</sup> = 0.055 =  $\alpha_6$ ; *n*-C<sub>7</sub>H<sub>15</sub><sup>+</sup>/*n*-C<sub>7</sub>H<sub>16</sub><sup>+</sup> = 0.026 =  $\alpha_7$ ). For *n*-hexane, the corrected parent peak heights,  $\theta_i$  (for *n*-C<sub>6</sub>H<sub>14-j</sub>D<sub>j</sub>), were given by eq A4, where  $\beta = 0.0645$  was the experimentally

$$\theta_{14} = \phi_{14} - \phi_{13}\beta$$

$$\theta_{13} = \phi_{13} - \phi_{12}\beta$$

$$\theta_{12} = \phi_{12} - \phi_{11}\beta - \phi_{14}\alpha_6 - (1/14)\theta_{13}\alpha_6$$

$$\theta_{11} = \phi_{11} - \phi_{10}\beta - (13/14)\phi_{13}\alpha_6 - (2/14)\theta_{12}\alpha_6$$

$$\theta_j = \phi_j - \phi_{j-1}\beta - ((j+2)/14)\phi_{j+2}\alpha_6 -$$

$$((13-j)/14)\theta_{j+1}\alpha_6 \quad (j = 3-12)$$

$$\theta_2 = \phi_2 - (\phi_1 - \phi_0\beta)\beta - (4/14)\theta_4\alpha_6 - (11/14)\theta_3\alpha_6 - \phi_0\beta'$$

$$\theta_1 = \phi_1 - \phi_0\beta - (3/14)\theta_3\alpha_6 - (12/14)\theta_2\alpha_6 \quad (A4)$$

determined correction factor for <sup>13</sup>C,  $\alpha_6 = 0.055$  was the *n*-C<sub>6</sub>H<sub>13</sub><sup>+</sup>/*n*-C<sub>6</sub>H<sub>14</sub><sup>+</sup> peak height ratio, and  $\beta' = 0.00162$  was the correction factor for two <sup>13</sup>C atoms in unreacted *n*-hexane. A similar series of equations can be derived easily for isobutane ( $\beta = 0.042$ ,  $\alpha_4 = 0.89$ ,  $\beta' = 0.001$ ).

To illustrate the use of these correction procedures, Table V summarizes a series of example calculations for *n*-hexane-D<sub>2</sub> 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 86–100 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 by using  $\gamma = 1.22 \times 10^{-3}$ . The third row summarizes  $\theta_i$  values that are corrected for carbon-13 and statistical cracking to alkyl cations by using eq A4. The fourth row lists  $d_i$  values, and the fifth row summarizes the initial exchange product distribution (mol %).

**Registry No.** Isobutane, 75-28-5; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; Pt, 7440-06-4; H<sub>2</sub>, 1333-74-0.

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(21) D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969.