Deuterium Tracer Study of the Conversion of Methylcyclohexane/*n*-Octane Mixtures with Pt/SiO_2 and Pt/Al_2O_3 Catalysts

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Hydrogen/deuterium exchange has been determined for mixtures of *n*-octane-d_{18}/methylcyclohexane-d_0 and *n*-octane-d_0/methylcyclohexane-d_{14} as well as *n*-octane-d_0/methylcyclohexane-d_0/D_2 at low (300–400°C) and high (482°C) temperatures. H/D exchange occurred in both reactants and products at the low temperatures. At 482°C, exchange did not occur in the reactants but did occur in the products. The results are consistent with the high temperature conversions occurring by a mechanism with a rate-limiting step of adsorption of the reactant. © 1994 Academic Press, Inc.

INTRODUCTION

Alkane conversion to aromatics occurs during catalytic reforming of paraffinic naphthas into high octane fuels. The mechanism of this reaction has proven to be more complex than many early investigators realized. Whether the reaction involves cyclization followed by dehydrogenation or whether it is dehydrogenation followed by cyclization remains open to debate even today (1). Furthermore, the identity of the elementary reactions on the surface of the metal and which step is rate-determining are still not fully understood.

In these hydrocarbon reactions, hydrogen may impact the reaction. For example, Paál and Menon (2) indicate that at high pressures, hydrogen adsorbed on active sites may diminish the number of sites available for the cyclization of hydrocarbons. Paál has studied the role of hydrogen on the selectivity of the conversion of hexane (3–6) as well as the role of hydrogen in the sintering of a platinum catalyst (7–9). The dehydrocyclization of alkanes has been considered to be impacted by a virtual surface hydrogen pressure which may differ significantly from the gas phase hydrogen pressure (10, 11).

Iglesia *et al.* (10, 11) studied the conversion of alkanes with a Te–Na*X* catalyst using ^{13}C-labeled heptane. The data indicated that the olefin, diene, and triene species were the reactive intermediates, and cyclization of the triene occurred in the gas phase. Furthermore, the sequential dehydrogenation rates were limited by a hydrogen desorption step that resulted in high surface pressures of hydrogen. These authors indicated that the nonmetal catalyst differ from the noble metal catalysts with respect to the ring closure aspect of the dehydrocyclization.

Most paraffin dehydrocyclization studies have been conducted with a pure compound. Both ^{14}C- and ^{13}C-labeled compounds have been used in mechanistic studies. Competitive conversions may provide more information about the reaction and more closely resemble naphtha reforming. In a study of the competitive conversion of paraffin and naphtane mixtures, it was found that at 400°C, the relative rates of conversion were as expected, with the naphthene being converted much more rapidly (12). Thus, at 400°C, the cycloalkane was converted at least 20 times more rapidly than the paraffin; furthermore, this was considered to be a lower limit because the nearly complete conversion of the cycloalkane made it difficult to obtain an accurate measure of the relative conversion. At a reaction temperature of 482°C, the situation was quite different; the relative conversion of the naphthene and the paraffin was nearly equal to the relative molar concentration of each reactant in the feed. Thus, for a feed consisting of an equal molar concentration of methylcyclohexane and *n*-octane, the cycloalkane underwent conversion at only about 1.2–1.4 times more rapidly than the *n*-alkane.

Two extreme adsorption models were considered for the competitive conversion of naphthene and paraffin: (1) a competitive, reversible adsorption and (2) a competitive, irreversible adsorption (12). In the case of model (1) for Langmuir–Hinshelwood-type adsorption of naphthene (N) and paraffin (P) on a surface (S) we have

$$\mathrm{N} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{NS} \qquad [1]$$

$$\mathrm{NS} \xrightarrow{k_2} \text{Products} + \mathrm{S} \qquad [2]$$

$$\mathrm{P} + \mathrm{S} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{PS} \qquad [3]$$

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$$PS \xrightarrow{k_4} \text{Products} + S \quad [4]$$

$$\theta_N = K_N P_N/(1 + K_N P_N + K_P P_P) \quad [5]$$

$$\theta_P = K_P P_P/(1 + K_N P_P + K_P P_P), \quad [6]$$

where $K_N = k_1/k_{-1}$ and $K_P = k_3/k_{-3}$. Since

$$d(\text{N})/dt = k_2\theta_N \quad [7]$$

and

$$d(\text{P})/dt = k_4\theta_P, \quad [8]$$

we have

$$d(\text{N})/d(\text{P}) = k_2\theta_N/k_4\theta_P = K_N k_2 P_N/K_P d_4 P_P. \quad [9]$$

In the case of an equalmolar reactant mixture ($P_N = P_P$) and equal adsorption constants ($K_N = K_P$), the relative conversion of N and P becomes

$$d(\text{N})/d(\text{P}) = k_2/k_4. \quad [10]$$

Thus, when this model is applicable, it is expected that the naphthene should be converted much more rapidly than the paraffin, since $k_2 \gg k_4$.

For the second model, which is based on irreversible adsorption, each reactant will attain a steady state surface concentration. Thus, the surface coverage will have the form

$$\theta'_N = K'_N P_N/(1 + K'_N P_N + K'_P P_P), \quad [11]$$

$$\theta'_P = K'_P P_P/(1 + K'_N P_N + K'_P P_P), \quad [12]$$

where

$$K'_N = k_1/(k_{-1} - k_2) \quad \text{and} \quad K'_P = k_3/(k_{-3} - k_4). \quad [13]$$

Then,

$$d(\text{N})/d(\text{P}) = k_2\theta_N/k_4\theta_P = k_2 K'_N P_N/k_4 K'_P P_P. \quad [14]$$

The condition of irreversible adsorption requires $k_2 \gg k_{-1}$ and $k_4 \gg k_{-3}$ so that

$$d(\text{N})/d(\text{P}) = k_2[k_1/(k_{-1} - k_2)]P_N/k_4[k_3/(k_{-3} - k_4)]P_P \quad [15]$$

$$= k_2(k_1/k_2)P_N/k_4(k_3/k_4)P_P \quad [16]$$

$$= k_1 P_N/k_3 P_P. \quad [17]$$

For an equimolar reaction mixture, $P_N = P_P$ so that

$$d(\text{N})/d(\text{P}) = k_1/k_3. \quad [18]$$

For an equal adsorption probability of the naphthene and paraffin, $k_1/k_3 = 1$ so that

$$d(\text{N})/d(\text{P}) = 1. \quad [19]$$

Likewise, if the irreversible adsorption condition is correct, the conversions in which $P_N \neq P_P$ will be directly related to the ratio of the two reactants, so that in this case,

$$\frac{d(\text{N})}{d(\text{P})} = \frac{P_N}{P_P}. \quad [20]$$

It should be possible to use deuterium gas or deuterium-labeled reactants to learn whether the surprising result of the competitive conversions at these temperatures is due to differences in the reversibility of the adsorption. For example, for reversible adsorption at lower temperatures, the incorporation of deuterium, added with the hydrogen containing reactants, into the reactants as well as products is expected. For irreversible adsorption, deuterium should not be incorporated into the reactants. The present study was undertaken to learn whether the anticipated exchange results are obtained.

EXPERIMENTAL

The reaction was carried out in a conventional flow apparatus described previously (13). Runs were effected at atmospheric pressure and a liquid (LHSV) of 1.0, unless noted otherwise in the Results section. Liquid samples were collected at intervals and analyzed by gas chromatography using a DB-5 column. The deuterium content was obtained using a GC/MS at 10 or 70 eV; the gas chromatograph was interfaced with an HP5971A mass selective detector that was operated under the control of a Vectra 05/165 computer using HPG1043B software.

n-Octane-d_{18}, methylcyclohexane-d_{14}, and D_2 gas were purchased from Cambridge isotope Laboratories and unlabeled materials were purchased from Aldrich Chemical Company, Inc. All of the reagents used in this study were 99% pure or higher and were used without further purification.

Catalysts

$Pt-SiO_2$ (1 wt% Pt) was prepared by the incipient wetness technique using an aqueous solution of H_2PtCl_6 and SiO_2 (200 mesh; 300 m^2/g) obtained from W. R. Grace.

$Pt-Al_2O_3-K$: "Nonacidic" alumina (12) was impregnated with chloroplatinic acid; the chloride content of the catalyst was reduced to a low level by washing the reduced catalyst with ammonium hydroxide. The catalyst contained 0.6 wt% Pt, 1 wt% K, and less than 0.05 wt% Cl.

RESULTS

The products from the conversion of a mixture of methylcyclohexane and *n*-octane on Pt–SiO_2 at 482°C are given in Table 1. The identities of the products listed in Table 1 were confirmed by GC/MS data. From the data in this table, it can be seen that toluene, ethylbenzene, and *o*-xylene are the major products; in addition, benzene, methylcyclohexene, octenes, octadienes, *p*-xylene, and *m*-xylene are also produced. The relative molar conversion of methylcyclohexane and *n*-octane is 1.17; this is in good agreement with values reported earlier (12).

If adsorption and desorption on the surface of the metal are reversible at 482°C for the reaction mixture of methylcyclohexane-d_0/*n*-octane-d_{18} or methylcyclohexane-d_{14}/*n*-octane-d_0, there should be evidence of D/H exchange in the recovered reactants. As can be seen from the data in Figs. 1 and 2, this is not the case. There is no detectable deuterium incorporated into methylcyclohexane and very little protium incorporated into *n*-octane-d_{18} in the case of the run with methylcyclohexane-d_0/*n*-octane-d_{18}. Likewise, there is very little protium incorporation in the recovered methylcyclohexane-d_{14} and very little deuterium incorporation in the *n*-octane-d_0 in the case of the methylcyclohexane-d_{14}/*n*-octane-d_0 run. Similar results, i.e., the lack of D incorporation, were obtained in the case of experiments with a methylcyclohexane/*n*-octane/D_2 feed.

TABLE 1

Product Distribution for the Conversion of a Methylcyclohexane/*n*-Octane[a] Mixture with Pt–SiO_2 at 482°C

Compounds	Wt%
Benzene	0.44
Methylcyclohexane[b]	19.9
Methylcyclohexene	0.52
Toluene	39.1
Octane[c]	27.4
1-Octene	1.33
2-Octene	0.76
Octadiene	0.20
Ethylbenzene	4.06
p,*m*-Xylene	0.19
o-Xylene	4.07

[a] Starting mixture: methylcyclohexane, 61.1 mole%; *n*-octane, 38.9 mole%.

[b] The conversion of methylcyclohexane is 65.4%.

[c] The conversion of *n*-octane is 35.5%. The conversion ratio of methylcyclohexane/*n*-octane is 1.85; correcting to an equal molar basis makes the ratio 1.17.

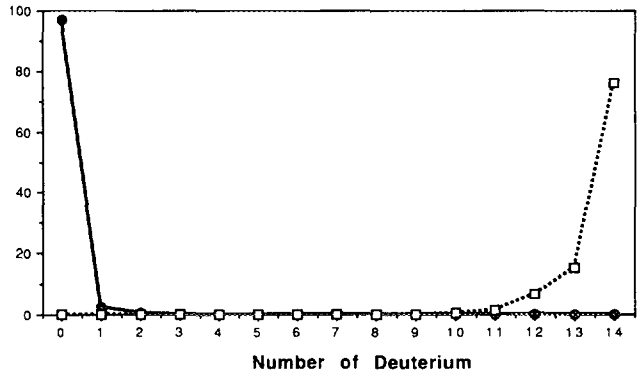


FIG. 1. Deuterium incorporation into methylcyclohexane at 482°C using a Pt–SiO_2 catalyst: (●) *n*-octane-d_{18}/methylcyclohexane-d_0, and (□) methylcyclohexane-d_{14}/*n*-octane-d_0.

These results indicate that almost all of the reactants adsorbed onto the surface of metal at 482°C were converted to products and that an adsorption/desorption equilibrium was not established under these conditions.

Different temperatures were used for the conversion of a mixture of methylcyclohexane-d_{14} (~12 mole%)/*n*-octane-d_0 (~88%) over Pt–SiO_2. The data (Table 2 and Fig. 3) show that H/D exchange increases in the unconverted reactants as the temperature decreases. For methylcyclohexane-d_{14}/*n*-octane-d_0 at 482°C, there is about 10% methylcyclohexane-h_1 and 5% methylcyclohexane-h_2 in the unconverted methylcyclohexane-d_{14} with the remainder being unexchanged h_0. At 375°C, protium incorporation was higher, producing exchange products up to h_4 (1%). In contrast, for conversions at 300°C, the recovered methylcyclohexane consists of a mixture of H_0 to H_{14} components. In the case of *n*-octane-d_0/methylcyclohexane-d_{14} at 482°C, less than 2% *n*-octane-d_1 is formed; the remainder is *n*-octane-d_0. At 375°C, the deuterium incorporation increased and was present up to *n*-octane-d_3 (1%). At 300°C, the most abundant *n*-octane species are *n*-$C_8H_{17}D$, *n*-$C_8H_{16}D_2$, and *n*-$C_8H_{15}D_3$, and significant

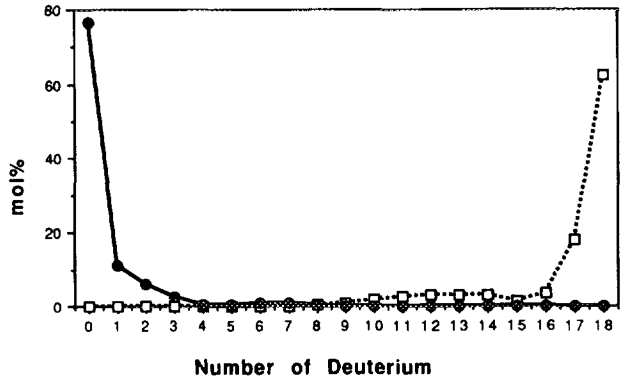


FIG. 2. Deuterium incorporation into *n*-octane at 482°C using a Pt–SiO_2 catalyst: (□) *n*-octane-d_{18}/methylcyclohexane-d_0, and (●) methylcyclohexane-d_{14}/*n*-octane-d_0.

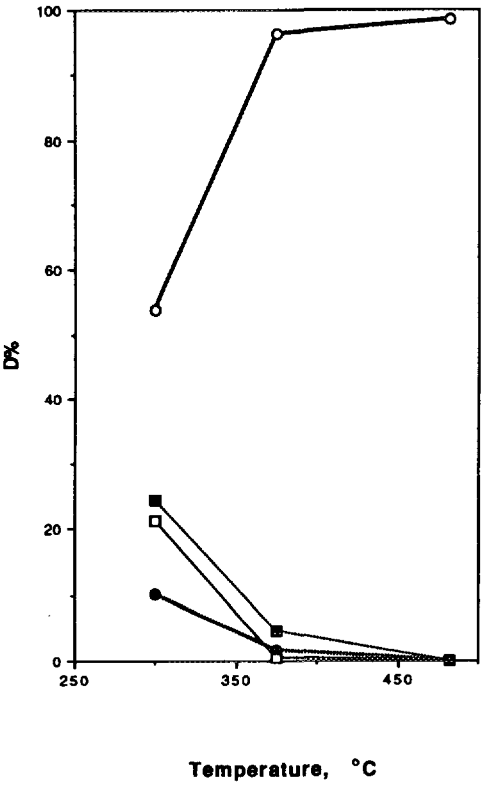


FIG. 3. Deuterium percentage in octane and methylcyclohexane from runs at different temperatures: (○) methylcyclohexane (methylcyclohexane-d_{14}/n-d_0 run), (●) octane (n-octane-d_0/methylcyclohexane-d_{14} run), (□) methylcyclohexane (methylcyclohexane-d_0/n-octane-d_0/D_2 run), and (■) n-octane (methylcyclohexane-d_0/n-octane-d_0/D_2 run).

amounts of species up to n-$C_8H_{12}D_6$ were also observed. These results show that both the rate of isotope exchange and the depth of exchange increased as the temperature decreased.

Similar results were obtained when a mixture of methylcyclohexane and n-octane was passed over the catalyst together with D_2 gas. As shown in Fig. 3, as the temperature decreases, the incorporation of deuterium into the reactants increases.

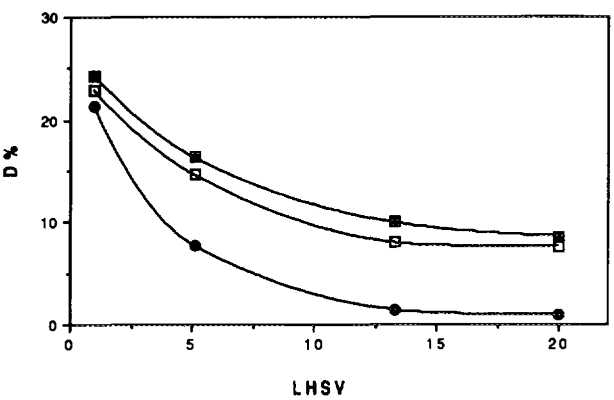


FIG. 4. Deuterium percentage in reactants and toluene products for runs at 300°C with a Pt–SiO_2 catalyst with deuterium gas present: (●) methylcyclohexane, (□) toluene, and (■) n-octane.

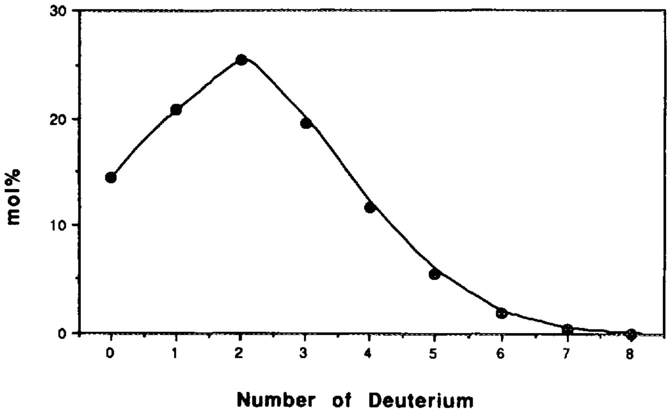


FIG. 5. Deuterium distribution in toluene produced in methylcyclohexane/n-octane/D_2 run using a Pt–SiO_2 catalyst at 482°C.

For runs at 300°C, the flow rate was adjusted to keep the methylcyclohexane conversion to ~30% or lower. In this case, even though ethylbenzene and o-xylene were not detected, significant amounts of deuterium were incorporated into the recovered n-octane (Fig. 4). The deuterium incorporation, as expected, decreased as the flow rate increased from 1 ml/h to 20 ml/h. Deuterium was also incorporated into the unreacted methylcyclohexane, but the amount of incorporation becomes smaller than that for n-octane as the flow rate increases.

H or D was incorporated in all products in all runs. Because there was essentially no H/D exchange in the starting reagents for runs at 482°C, any H/D incorporated into toluene or ethylbenzene at this temperature can be considered to be the result of exchange on the surface as the reactant is converted to the aromatic. The data in Table 3 show that the percent of H in ethylbenzene is 2.4 times that of the percent of D in toluene for the run with Pt–SiO_2 at 482°C with the methylcyclohexane-d_0/n-oc-

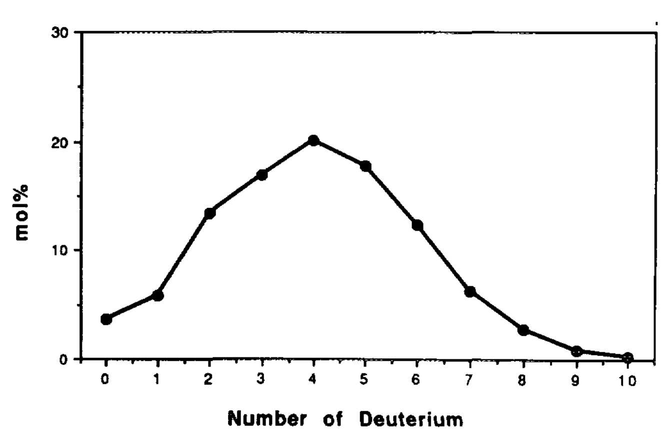


FIG. 6. Deuterium distribution in ethylbenzene produced in methylcyclohexane/octane/D_2 run with Pt–SiO_2 catalyst at 482°C.

TABLE 2

Deuterium Incorporation in the Starting Reagents Using a Pt–SiO$_2$ Catalyst

Deuterium content	Methylcyclohexane					*n*-Octane				
	300°C		375°C	482°C		300°C		375°C	482°C	
	A	B	A	A	B	A	B	A	A	B
d_0	1.44	4.15	—	—	94.5	15.0	1.09	78.1	98.2	74.4
d_1	3.68	13.6	—	—	4.74	29.2	4.49	16.4	1.53	8.39
d_2	4.90	21.3	—	—	0.59	28.0	10.6	4.39	0.29	4.21
d_3	6.09	24.4	—	—	0.16	17.3	17.1	0.97	—	3.44
d_4	7.68	19.3	—	—	—	7.46	20.4	0.15	—	3.04
d_5	7.48	12.1	0.08	—	—	2.39	19.1	—	—	2.35
d_6	8.32	4.57	0.14	—	—	0.58	13.8	—	—	1.77
d_7	8.64	0.59	0.24	—	—	—	8.06	—	—	1.26
d_8	8.61	—	0.43	—	—	—	3.56	—	—	0.75
d_9	9.29	—	0.54	—	—	—	1.31	—	—	0.36
d_{10}	8.71	—	0.93	0.16	—	—	0.40	—	—	—
d_{11}	8.79	—	2.01	0.59	—	—	—	—	—	—
d_{12}	8.10	—	7.02	4.93	—	—	—	—	—	—
d_{13}	5.49	—	16.9	9.54	—	—	—	—	—	—
d_{14}	2.77	—	71.7	84.76	—	—	—	—	—	—
d_{15}						—	—	—	—	—
d_{16}						—	—	—	—	—
d_{17}						—	—	—	—	—
d_{18}						—	—	—	—	—

Note. A: Mixture of methylcyclohexane-d_{14} (12%) and *n*-octane-d_0 (88%). B: Mixture of methylcyclohexane (56.3%) and *n*-octane (42.9%) and D_2 gas (8.5 ml/min).

TABLE 3

Deuterium Incorporation in the Aromatic Products Formed at 482°C Using Pt–SiO$_2$

Deuterium number	Toluene			Ethylbenzene		
	A	B	C	A	B	C
d_0		1.04	25.4	1.05	3.72	2.31
d_1		6.59	20.3	1.50	11.9	4.63
d_2	35.7	7.02	23.4	3.82	22.9	8.88
d_3	29.0	0.37	15.2	6.92	26.2	14.4
d_4	18.8	6.87	8.75	10.4	19.9	19.5
d_5	9.76	31.6	4.80	12.5	10.2	20.7
d_6	4.38	24.5	1.56	15.0	3.65	16.0
d_7	1.87	14.7	0.40	17.0	1.06	8.77
d_8	0.54	7.26	0.06	16.6	0.27	3.41
d_9	0.07			10.7	0.15	1.06
d_{10}	0.01			4.47	0.10	0.36
H%	84.2	35.5	77.0	38.3	70.0	55.6
D%	15.8	64.5	23.0	61.7	30.0	44.4

Note. A: Starting reagents are methylcyclohexane-d_0 (57.2%) and *n*-octane-d_{18} (42.3%) mole or wt%. B: Starting reagents are methylcyclohexane-d_{14} (57.2%) and *n*-octane-d_0(42.3%). C: Starting reagents are methylcyclohexane-d_0(56.3%), *n*-octane-d_0 (42.9%), and D_2 gas (8.5 ml/min).

TABLE 4

Deuterium Incorporation in the Products and the Starting Reagents in Pt–Al_2O_3 and Alumina Runs

Catalyst	Al_2O_3–A[a]	Al_2O_3–B[b]	Al_2O_3–B[b]	Pt–Al_2O_3	Pt–Al_2O_3	Pt–Al_2O_3
Reagents						
MCH (wt%)	55.2 (d_0)	55.2 (d_0)	57.2 (d_0)	55.2 (d_0)	55.2 (d_0)	47.0 (d_0)
Octane (wt%)	43.6 (d_{18})	43.6 (d_{18})	42.3 (d_0)	43.6 (d_{18})	43.6 (d_{18})	53.0 (d_0)
D_2 (mL/min)	—	—	6.0	—	—	6.0
Temp (°C)	482	482	482	482	425	482
Conversion						
MCH (%)	8.0	9.1	1.2	70.14	12.30	67.98
Octane (%)	3.7	0.3	<0.5	45.09	4.94	33.36
Products (H/D)						
MCH						
H%	66.0	80.0	84.2	87.2	94.2	96.9
D%	34.0	20.0	15.9	12.8	5.8	3.3
Toluene						
H%	65.3	68.7	70.1	59.0	60.3	64.9
D%	34.7	31.4	29.9	41.0	39.7	35.1
Octane						
H%	37.0	37.4	84.6	35.0	14.7	86.3
D%	63.0	62.6	15.4	65.0	85.3	13.7
Ethylbenzene						
H%	59.7	67.7	68.2	55.6	55.0	68.5
D%	40.3	32.3	31.9	44.4	45.1	31.6

[a] Acidic alumina.

[b] Nonacidic alumina containing about 1% K.

taned$_{18}$ mixture. The percent of D in ethylbenzene is about the same as the percent of H in toluene in the case of the run with methylcyclohexane-d_{14}/*n*-octane-d_0. Because the H/D ratio on the surface of the metal is not known in these two runs, quantitative conclusions from the above two experiments are difficult to make. In the case of the run with methylcyclohexane/*n*-octane/D_2, the surface H/D ratio must be the same for the toluene and the ethylbenzene. In this case, the percent of D in tolue is 23 and the percent of D in ethylbenzene is 44. As can be seen from Figs. 5 and 6, the highest deuterium containing molecule in toluene is d_2. However, in the case of ethylbenzene, the deuterium incorporation is almost a statistical distribution centered at d_4. Combining this results obtained from the runs with methylcyclohexane-d_0/*n*-octane-d_{18} and methylcyclohexane-d_{14}/*n*-octane-d_0, it can be concluded that the behavior of methylcyclohexane and *n*-octane during product formation process is different, since about 1.9 times more deuterium is incorporated into ethylbenzene than into toluene.

Deuterium tracer experiments were conducted using

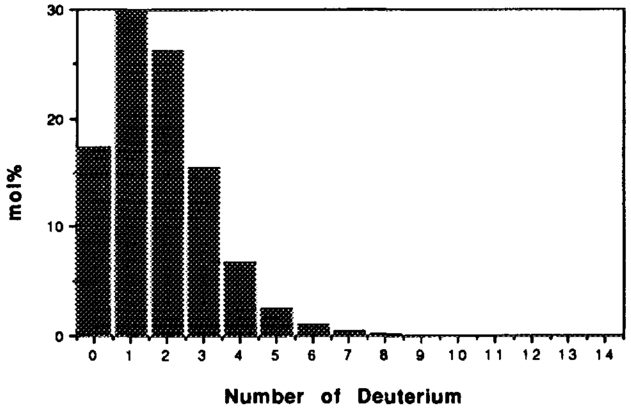


FIG. 7. Deuterium distribution in methylcyclohexane in products from a run at 482°C using a Pt–Al_2O_3 catalyst.

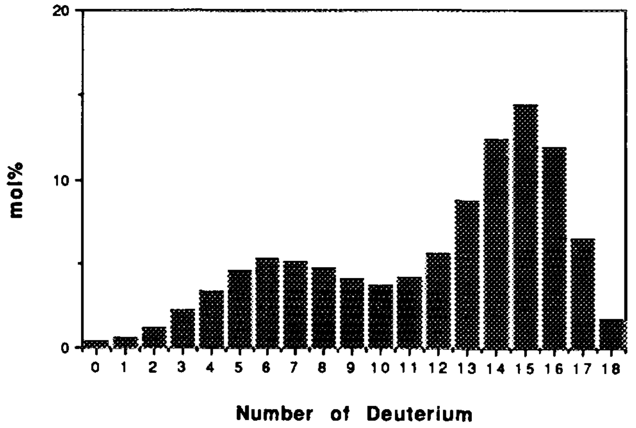


FIG. 8. Deuterium distribution in *n*-octane in products from conversion of *n*-octane-d_{18}—methylcyclohexane-d_0 at 482°C with a Pt–Al_2O_3 catalyst.

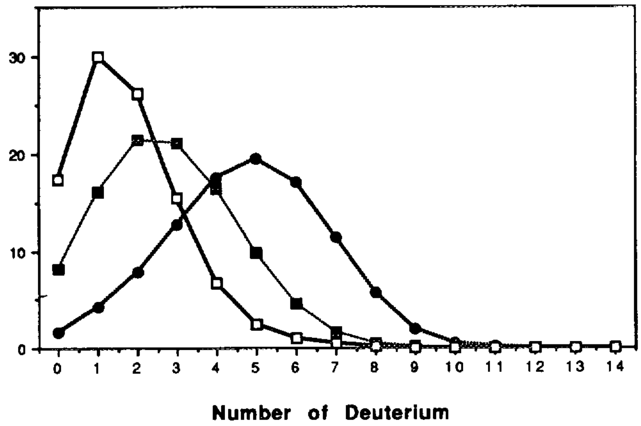


FIG. 9. Deuterium incorporation in methylcyclohexane with *n*-octane-d_{18}/methylcyclohexane-d_0 in runs at 482°C with (□) Pt–Al_2O_3, (◆) nonacidic Al_2O_3 containing about 1% K, and (●) acidic Al_2O_3.

Pt–Al_2O_3 as well as an acidic and a nonacidic alumina that did not contain Pt. The results are given in Table 4. At both 425 and 482°C on Pt–Al_2O_3, deuterium was incorporated into the recovered methylcyclohexane with species up to d_9 and protium was incorported into *n*-octane-d_{18} up to *n*-octane-h_{18} (Figs. 7 and 8). For the runs using only alumina where the conversion to aromatic is very low, the H/D exchange in the recovered reactants is about the same as for the run with the Pt–Al_2O_3 catalyst (Figs. 9 and 10). For runs at 482°C with the Pt–Al_2O_3 catalyst, it appears that the H/D exchange reaction occurs primarily on the alumina support. SiO_2 differs from alumina in this respect. The methylcyclohexane/*n*-octane mixture was passed over SiO_2 together with D_2. At both 300 and 482°C, there is no H/D exchange in the reactants. It is therefore clear that the exchange reaction occurs on the surface of Pt in the runs with the Pt–SiO_2 catalyst, but in the case of the Pt–Al_2O_3 catalyst, exchange occurs on both the alumina and Pt surface, with the alumina-catalyzed exchange dominating that of the Pt-catalyzed exchange.

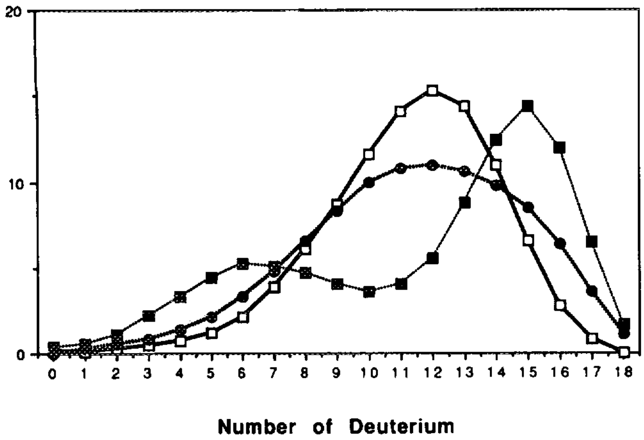


FIG. 10. Protium incorporation in octane for conversion of *n*-octane-d_{18}/methylcyclohexane-d_0 at 482°C with Pt–Al_2O_3 (□), nonacidic Al_2O_3 containing about 1% K. (◆), and acidic Al_2O_3 (●).

DISCUSSION

The isotope exchange properties of silica and alumina supports are different. At 482°C, alumina is very active for H/D exchange either in the presence or absence of gaseous hydrogen (deuterium). Thus, deuterium and hydrogen are incorporated into alkanes and cycloalkanes by H/D exchange between C_7H_{14} and C_8D_{18} and vice versa. Silica, on the other hand, does not catalyze exchange to a measurable extent between either hydrocarbons or gaseous hydrogen (or deuterium) and hydrocarbons. Even with a "nonacidic" alumina that contains 1.0 wt% K, there is extensive incorporation of deuterium from gaseous D_2 into both methylcyclohexane and *n*-octane. It can be argued that Brønsted acid sites are responsible for the exchange with the acidic alumina; however, the 1 wt% K should be sufficient to eliminate Brønsted acidity with the "nonacidic" alumina. Thus, the exchange catalyzed by the nonacidic alumina is presumably due to coordinately unsaturated sites or Lewis sites. These latter sites, if present on silica, must be much less active than those on alumina.

The deuterium distribution (Fig. 9) in methylcyclohexane is striking at first glance. It appears that deuterium exchanges with hydrogen in methylcyclohexane at 482°C more rapidly with the alumina support than with a Pt–alumina catalyst. However, because of the dehydrogenation reaction catalyzed by Pt, part of the exchanged methylcyclohexane undergoes dehydrogenation to toluene, and this may account for the smaller extent of exchange. The data do show, however, that the alumina support is an effective catalyst for hydrogen/deuterium exchange in hydrocarbons at these high temperatures. Alumina has been shown to be a catalyst for deuterium exchange with hydrogens in hydrocarbons at lower temperatures but not necessarily at the low contact time that is used in this study (for example, Ref. (14)). The data for *n*-octane (Fig. 10) are also consistent with this. Deuterium/hydrogen exchange is more extensive with *n*-octane than with methylcyclohexane. For both acidic and nonacidic alumina, the most abundant exchange species is $C_8H_6D_{12}$; however, there is a wide distribution of values of x for the isotopically labeled $C_8H_{18-x}D_x$.

Even in the absence of Pt, alumina catalyzes at 482°C the formation of minor amounts of toluene and ethylbenzene/*o*-xylene from methylcyclohexane and *n*-octane, respectively. The deuterium distributions in each of these aromatic compounds are similar for the two alumina supports and for the Pt–alumina catalyst. The distribution in ethylbenzene, centered at about $C_8H_3D_5$, is consistent with the aromatization of *n*-octane that involves a statistical removal of hydrogen/deuterium from *n*-octane with a distribution centered at $C_8H_6D_{12}$. Likewise, the distribution of deuterium in toluene is consistent with the statistical removal of hydrogen/deuterium from methylcyclohexane.

There was little difference in the H/D distributions in the reactants or products for the runs with the $Pt-Al_2O_3$ catalyst and the acidic or nonacidic alumina. Thus, it is apparent that the alumina-catalyzed exchange reaction dominates the overall exchange process with a $Pt-Al_2O_3$ catalyst. For the exchange of C_8D_{18} with C_7H_{14}, it appears that the label in *n*-octane may consist of two exchange processes, since there are two maxima in the curves shown in Fig. 10. However, if Pt behaves on alumina as it does on silica, neigher of these distributions would be due to the metal itself.

The nearly equal conversion of naphthene and alkane with the Pt containing catalysts could occur if desorption of the aromatic products was the rate-limiting step. The fact that both the octenes and the aromatics undergo extensive exchange while the reactants do not is considered to eliminate desorption as the rate-limiting step. If desorption was the rate-limiting step, the alkane reactant should have undergone exchange.

If exchange occurs in methylcyclohexane and *n*-octane with the $Pt-SiO_2$ catalyst at 482°C, the reactant must be adsorbed in an activated state that would allow C–H bond breaking. However, the absence of exchange in the methylcyclohexane reactant at 482°C could be explained if the dehydrogenation reaction rate increases with temperature so that the ratio of the rate of dehydrogenation reaction to the exchange reaction becomes large. However, this explanation cannot be used to explain the results with *n*-octane nor the decrease in the extent of conversion of methylcyclohexane when *n*-octane is present.

For the conversions at 482°C, both toluene and C_8 aromatics contain H/D distributions that approach, or are at, a statistical H/D distribution (Figs. 5 and 6). This observation is true when the deuterium is present in *n*-octane, methylcyclohexane, or deuterium gas. Thus, the adsorbed species that leads to an aromatic hydrocarbon undergoes multiple exchange steps while it is on the surface of the platinum. This observation, together with essentially no exchange in either reactant, provides conclusive evidence that the reactants are both irreversibly adsorbed at 482°C. Thus, the deuterium tracer studies confirm the earlier postulate of irreversible adsorption (12).

Weinberg (15) recently reviewed much of his work on alkane activation on transition-metal surfaces. He described his results using a one-dimensional potential diagram as illustrated in Fig. 11. This figure represents a simpler case than that which is encountered in the present experiments, since the reactions were carried out at lower temperatures, and the only reaction allowed for the low carbon number alkanes was H/D exchange. The results do stress two important mechanistic considerations: (1) a physical adsorption precursor state is important, and (2) for Pt, in contrast to Ir, the exchange reaction has a higher activation energy than desorption does. Not emphasized is that the slow step of the exchange reaction in Fig. 11 is the recombination of the surface hydrocarbon radical and the surface H(D) atom.

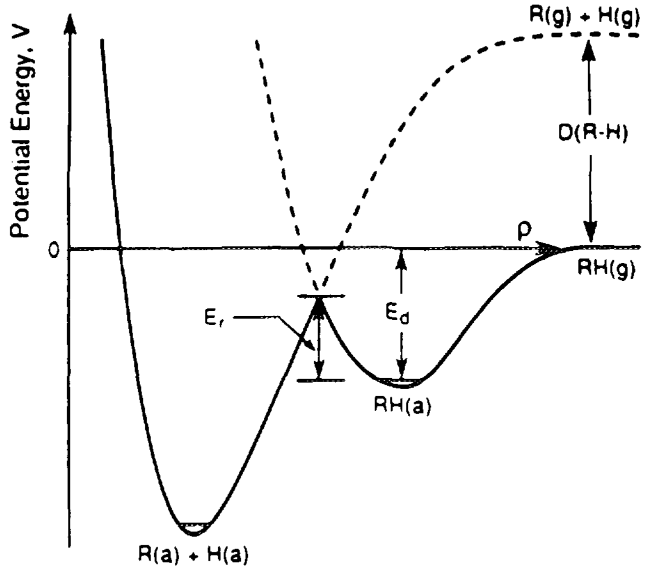


FIG. 11. Potential energy curve for exchange of deuterium with propane with Pt and Ir catalysts (redrawn from Ref. (15)).

For simplicity, we first consider only the potential energy diagram for alkane dehydrocyclization and exchange. A schematic potential energy diagram that is in agreement with the experimental observations is shown in Fig. 12. The initial adsorption to produce R· + H· is the same as that shown in Fig. 11. The important features for *n*-octane dehydrocyclization are the steps following the formation of the alkyl radical and the temperature dependence of these steps. In this discussion, we postulate that the next species formed in the dehydrocyclization pathway is an alkylidene-type species, although it is not required that this be the actual intermediate for the energy arguments to be valid. The formation of the next species from the adsorbed radical (the postulated alkylidene species) must have an activation energy that is very temperature dependent. Thus, at about 400°C and lower, the low temperature activation energy for exchange, $E_x)_l$, is much smaller than the activation energy for dehydrocyclization, $E_{dehyd})_l$ so that exchange of H/D readily occurs as shown by Weinberg (15) and by the data in the present study. However, the situation is reversed at the higher temperature of 482°C; here, the activation energy for dehydrocyclization, $E_{dehyd})_h$, is lower than the activation energy

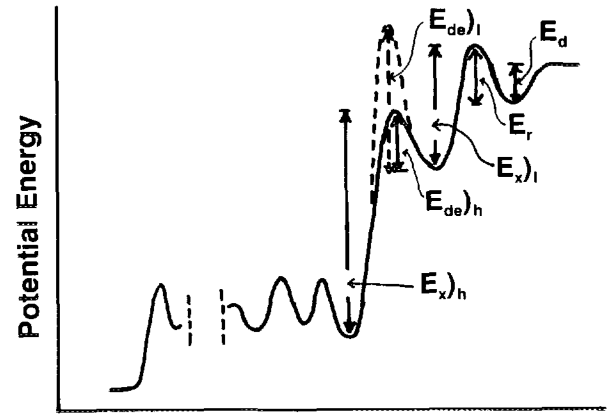


FIG. 12. Schematic potential energy diagram for the conversion of *n*-octane at low (l) and high (h) temperatures: E_d, activation energy for desorption of *n*-octane; E_r, activation for R-H → $R\cdot$ + H·; $E_x)_l$, activation energy for H/D exchange at low temperatures; $E_x)_h$, activation energy for H/D exchange at high temperatures; $E_{de})_l$, activation energy for $R\cdot \rightarrow R\colon$ + H· at low temperature; and $E_{de})_h$, activation energy for $R\cdot \rightarrow R\colon$ + H· at high temperature.

for exchange $E_x)_l$ (for simplicity we do not include the slight temperature dependence for $E_x)_l$ in Fig. 12 that was observed by Weinberg (15)). Thus, in the mechanism proposed for dehydrocyclization, the important feature is the relative activation energies between the formation (and its reverse reaction) of the adsorbed radical and the subsequent intermediate, the proposed alkylidene intermediate. At lower temperatures $E_x)_l < E_{dehyd})_l$ and H/D exchange readily occurs; at higher temperatuers $E_x)_h > E_{dehyd})_h$ so that this, combined with a large $E_x)_h$, prohibits desorption of the alkane compared to the subsequent reactions leading to the production of gaseous aromatics. In Fig. 12, the details of the many steps following the formation of the alkylidene species have only been illustrated by a series of steps. However, the multiple exchanges in the alkene and aromatic products indicate that the activation energy of all of the subsequent steps, including the desorption of octenes and aromatics, must be small compared to $E_x)_h$, the activation energy for the high temperature exchange reaction.

Alkenes are observed as products in the high temperature dehydrocyclization studies at atmospheric pressure. Furthermore, the alkenes obtained in the present study at 482°C have undergone multiple H/D exchange reactions. These observations indicate that the activation energies for the formation of an adsorbed alkene from the adsorbed alkylidene intermediate and for both H/D exchange and alkene desorption to the gas phase are small compared to the one labeled $E_x)_h$ in Fig. 12.

The above scheme allows for the dehydrocyclization of *n*-alkane without H/D exchange in the reactant. A similar scheme could be proposed to account for the absence of significant exchange in the unconverted methylcyclohexane. However, there is another possibility. Since the six-membered ring already exists in the methylcyclohexane, dehydrogenation to toluene is a facile reaction compared to *n*-octane dehydrocyclization. Furthermore, the surface coverage by species derived from methylcyclohexane and *n*-octane will be inversely related to the rate constants for their formation of aromatics, k_2 and k_4, respectively, and

$$\theta_{\mathrm{MCH}}/\theta_{n\text{-}\mathrm{C}_8} = k_4/k_2. \qquad [21]$$

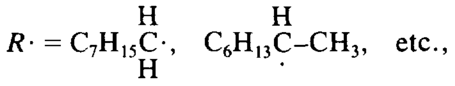
Thus, the much more rapid conversion of adsorbed methylcyclohexane, relative to *n*-octane, may decrease the residence time of the adsorbed methylcyclohexane to such a low level that exchange in methylcyclohexane becomes negligible compared to that in *n*-octane.

The proposed mechanism indicates that there should be a dependence of the ratio of the relative conversion fo methylcyclohexane and *n*-octane upon hydrogen pressure. This has been observed experimentally. Davis (12, 16) found that the conversion of methylcyclohexane was much greater than *n*-octane at both 200 and 400 psig. Others have also emphasized the important role of hydrogen in dehydrocyclization (6–10). Thus, it is anticipated that increasing the reaction pressure, for example, to 200 or 400 psig with the miture *n*-octane/methylcyclohexane/D_2 would lead to exchange in the reactants as well as the products. This exchange would arise by decreasing the concentration of the hydrocarbon radical, and especially the alkylidene intermediate, due to the high surface concentration of H atoms;

$$RH \rightleftarrows R\cdot + H\cdot \qquad [22]$$

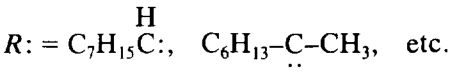
$$R\cdot \rightleftarrows R\colon + H\cdot, \qquad [23]$$

where



$$R\cdot = C_7H_{15}\overset{H}{\underset{H}{C}}\cdot, \quad C_6H_{13}\overset{H}{\underset{\cdot}{C}}\text{–}CH_3, \quad \text{etc.,}$$

and



$$R\colon = C_7H_{15}\overset{H}{C}\colon, \quad C_6H_{13}\text{–}\underset{\cdot\cdot}{C}\text{–}CH_3, \quad \text{etc.}$$

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