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Hydroisomerization and Hydrocracking of Alkanes

7. Influence of the Balance between Acid and Hydrogenating Functions on the Transformation of *n*-Decane on PtHY Catalysts

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The transformation of *n*-decane was studied at 473 K, 101 kPa and $p_{H_2}/p_{n\text{-decane}} = 9$ on a series of PtHY catalysts containing from 0.02 to 1.5 wt% platinum and with Si/Al atomic ratios of 3, 9, or 35. The ratio between the number of accessible Pt atoms and the number of acid sites on which the heat of ammonia adsorption is greater than 100 kJ mol^{-1} (n_{Pt}/n_A) was chosen for characterizing the balance between the hydrogenating and the acid functions. The activities, stabilities, and selectivities of the catalysts are definitely governed by this balance. For low values of n_{Pt}/n_A (<0.03), the activity per acid site is low, the deactivation is rapid and *n*-decane leads directly to all the isomerization and cracking products. For high values ($\geq$0.17) the activity per acid site is maximal, the deactivation is very slow and *n*-decane transforms successively into monobranched isomers, dibranched isomers, and tribranched isomers plus cracking products. In this latter case the catalyst can be considered as an *ideal* bifunctional catalyst, namely a catalyst on which only one transformation of the alkene intermediates on the acid sites can occur during their diffusion from the platinum sites on which they are generated to those on which they are hydrogenated. Therefore the reaction scheme of *n*-decane transformation matches the reaction scheme of olefinic intermediates. From the product distribution established on ideal catalysts the mechanism of the transformation of olefinic intermediates can be deduced. Branching isomerization occurs through protonated cyclopropane and cyclobutane intermediates. The cracking products result from the β-scission steps of tribranched decenes which involve two tertiary carbenium ion intermediates (mode A) and from the β-scission steps of dibranched decenes which involve one tertiary and one secondary carbenium ion intermediate (mode B). The participation of the β-scission of mono, di, and tribranched decenes through mode C (via two secondary carbenium ion intermediates) is negligible. The rate constants of the various steps involved in *n*-decane transformation are estimated. They can be classified in the following order:

A cracking > Methyl shift > Branching > B cracking $\gg$ C cracking.

INTRODUCTION

Bifunctional metal/acid zeolite catalysts are used in various industrial processes, viz., hydroisomerization of C_5–C_6 alkanes, hydrocracking, dewaxing, isomerization of the C_8 aromatic cut, etc. (1–3). On these catalysts the alkane transformation involves hydrogenation and dehydrogenation steps on the metallic sites, isomerization or cracking steps on the acid sites and diffusion steps of the olefinic intermediates from the acid to the metallic sites and vice versa. That is why their activity, stability, and selectivity depend on the characteristics of the acid and of the metallic sites, in particular on the balance between the acid and the hydrogenating functions (4–7), and on the characteristics of the zeolite pores (8–12). However, with large pore zeolites not exerting shape selectivity (e.g., Y zeolite), this latter effect can be neglected.

In the case of PtHY catalysts, it has been shown (8, 12, 14) that the balance between the acid and the hydrogenating functions could be characterized by the ratio of the number of hydrogenating sites to the number of acid sites (n_{Pt}/n_A). With *n*-heptane hydrocracking an ideal situation occurs for large values of n_{Pt}/n_A: the activity per acid site is maximal, the deactivation due to coking is very slow, and *n*-heptane is successively transformed into monobranched isomers, into dibranched isomers, then into cracking products (isobutane + propane). This reaction scheme matches the scheme of olefinic intermediate transformation on the acid sites, which allows us (i) to specify the mechanism of the various isomerization and cracking steps of olefins and (ii) to compare their rate, hence, the rate of the transformation of the carbenium ion intermediates.

However, heptane molecules are too small to be representative of the alkanes of an industrial hydrocracking feed. Therefore the effect of n_{Pt}/n_A on the rate, stability, and selectivity of hydrocracking must be confirmed for a longer molecule. For this reason *n*-decane hydrocracking has here been investigated on the series of PtHY catalysts previously

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used for n-heptane hydrocracking: platinum contents vary from 0.02 to 1.5 wt%, platinum dispersion greater than 70%, silicon to aluminum ratio of the HY zeolites equal to 3,9 and 35. Another advantage of n-decane hydrocracking is that all the possible modes of cracking of carbenium ions are involved, which was not the case with n-heptane hydrocracking (15). Indeed in this latter case there is no possible β-scission of a tertiary carbenium ion (mode A). As was the case with heptane hydrocracking, the apparent reaction scheme matches the scheme of olefinic intermediate transformation on PtHY catalysts with large values of n_{Pt}/n_A. From the product distribution established on these ideal catalysts for a large range of conversion (from 2 to above 80%), the mechanisms of the various steps of cracking and isomerization of olefinic intermediates are specified and their rates are compared.

TABLE 1

Physicochemical Characteristics of the Catalysts

Catalyst	Pt (wt%)	D (%)	n_{Pt}/n_A
[a] 0.02 PtHY3[b]	0.018	90	0.002
[a] 0.1 PtHY3[b]	0.07	90	0.006
[a] 0.2 PtHY3[b]	0.2	90	0.017
[a] 0.4 PtHY3[b]	0.35	80	0.029
[a] 1 PtHY3[b]	0.9	90	0.077
[a] 1.5 PtHY3[b]	1.5	70	0.10
[a] 1 PtHY9[b]	0.85	90	0.17
[a] 1 PtHY35[b]	1.0	90	0.48

Note. D = platinum dispersion; n_{Pt}-number of accessible platinum atoms; n_A number of strong acid sites.

[a] Pt, wt%.

[b] Si/Al ratio.

EXPERIMENTAL

Three HY zeolites were used: HY3, HY9, and HY35, with total silicon to aluminum ratios of 3, 9, and 35 (Si/Al framework ratios of 5, 10, and 40, estimated from the unit cell parameter (16)). HY3 was obtained by calcination of ultrastable NH_4Y at 773 K under a dry air flow, for 10 h. HY9 was obtained by $SiCl_4$ dealumination of NH_4Y (17) and HY35 by treatment of HY9 with 1*M* HCl at 373 K during 3 h. Their characteristics have already been reported (13). The acidities of the zeolites were characterized by NH_3 adsorption followed by microcalorimetry. The number of strong acid sites A, for which the heat of NH_3 adsorption was greater than 100 kJ mol^{-1} was equal to 34×10^{19}, 15×10^{19}, and 6×10^{19} g^{-1} for HY3, HY9, and HY35, respectively (5.9, 2.6, and 1.0 per unit cell).

The PtHY catalysts were prepared by ion exchange with $[Pt(NH_3)_4]Cl_2$ under the same conditions as those already described (18). The platinum content was determined by the "Centre d'Analyses CNRS de Solaize." In order to obtain a high dispersion of the platinum, the samples were calcined at 573 K under a dry air flow and treated under hydrogen flow at 773 K (14, 18). The platinum dispersion, estimated by transmission electron microscopy and/or by H_2–O_2 titration with a pulse system, was always greater than 70%. Both techniques gave comparable values. Table 1 presents the physicochemical characteristics of the PtHY catalysts.

The n-decane transformation was carried out at atmospheric pressure, in a flow reactor at 473 K, with a H_2/n-decane molar ratio of 9. The activities ((molar flow rate × conversion)/weight of catalyst) were measured at a conversion below 10%. The product distribution as a function of the conversion (from 2 to 80–95%) was obtained by modifying the contact time (50–500 mg of catalyst, 0.2–12 cm^3 h^{-1} of liquid n-decane). The reaction products were analyzed *on*-line by gas chromatography, using a polypropyleneglycol capillary column with 100 m length and 0.25 mm inner diameter.

RESULTS

1. Initial Activity and Stability

Figure 1 gives the initial activity A_0 (extrapolated to time-on-stream zero) of PtHY catalysts as a function of n_{Pt}/n_A, the ratio of the number of accessible platinum atoms to strong acid sites. For PtHY3 catalysts A_0 increases proportionally to n_{Pt}/n_A (hence to n_{Pt}) for low values of this ratio, then remains constant for $n_{Pt}/n_A > 0.03$. For identical values of n_{Pt}/n_A, 1 PtHY9 is 10 times less active and 1 PtHY35 is 200 times less active than PtHY3 catalysts.

The deactivation depends on n_{Pt}/n_A: thus A_f/A_0, the ratio of the final activity (A_f, measured after 3 h of reaction) to the initial activity increases with n_{Pt}/n_A, reaching a value of 1 for $n_{Pt}/n_A \geq 0.1$, i.e., for 1.5 PtHY3, 1 PtHY9, and 1 PtHY35 (Fig. 2).

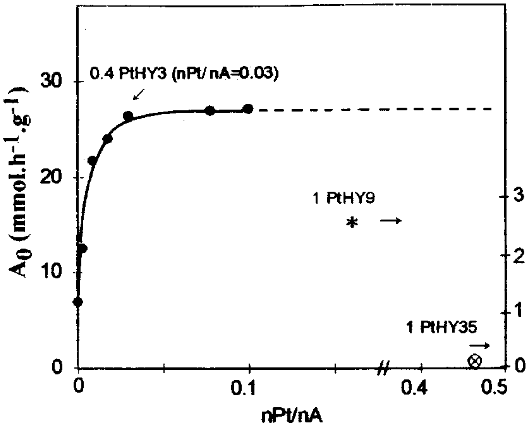


FIG. 1. Initial activity of PtHY catalysts (A_0) as a function of the ratio of platinum sites/acid sites (n_{Pt}/n_A).

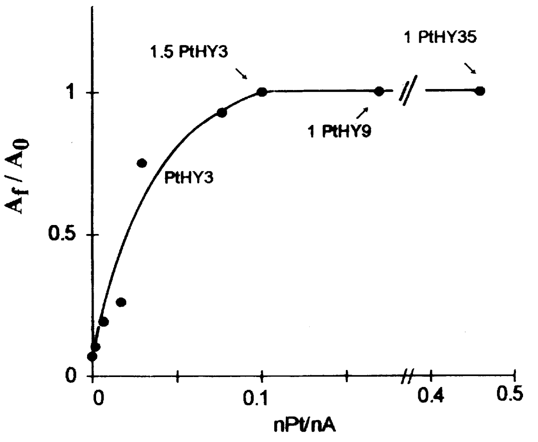


FIG. 2. Ratio of the final/initial activities of PtHY catalysts (A_f/A_0) as a function of the ratio of platinum sites/acid sites (n_{Pt}/n_A).

2. Product Distribution

Whatever the catalyst, *n*-decane leads to isomers (I) and to light products (C). The light products are only C_3–C_7 with all the catalysts except 1 PtHY35 for which C_1 and C_2 (hydrogenolysis products) are also observed. That is why with this catalyst only the selectivity to isomerization will be considered. The isodecanes obtained are essentially monobranched, M (methylnonanes, ethyloctanes, and propylheptane) or dibranched, B (dimethyloctanes and methylethylheptanes). Only four tribranched isomers (there are 25 trimethylheptanes and dimethylethylhexanes) could be separated from the dibranched isomers. These isomers were not identified. Observed in small amounts at high conversion, they will be included in B.

The product distribution depends on the catalyst and on the conversion. Figure 3 compares the distribution of C, M, and B as functions of the conversion for 0.1 PtHY3, 0.4 PtHY3, 1 PtHY3, and 1 PtHY9. With the two first catalysts M, B, and C products are directly formed; with 1 PtHY3 only the isomers M and B are primary products. With 1 PtHY9 and 1 PtHY35 and, probably, with 1.5 PtHY3, only the monobranched isomers M appear as primary products, the B isomers being formed for conversions above 10% and the cracking products C for conversions above 25%. On all the catalysts the ratio I/C of isomerized to cracked *n*-decane decreases when the conversion increases (Fig. 4a). The greater the n_{Pt}/n_A value of the catalyst the greater I/C. The yield in isomers ($I = M + B$) as function of the conversion passes through a maximum with all the catalysts (Fig. 4b). The maximum yield increases from 4% for 0.1 PtHY3

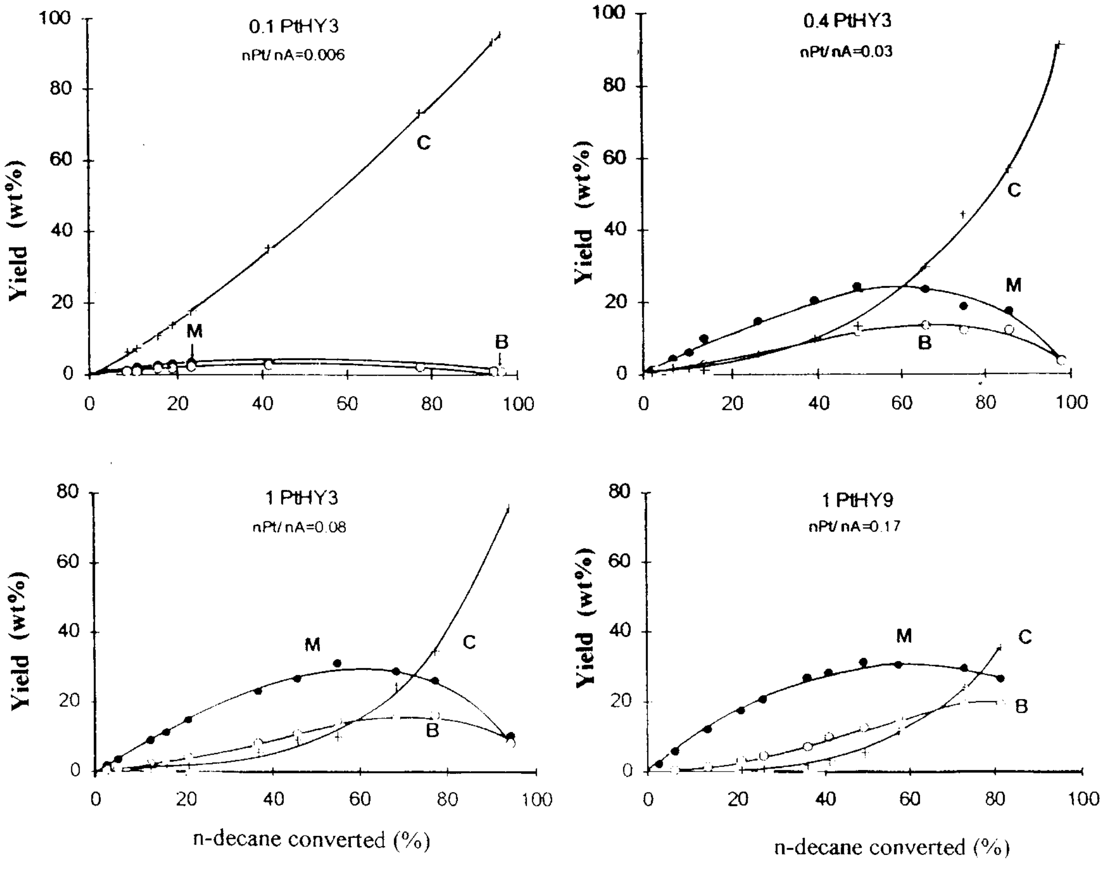


FIG. 3. Yields of monobranched isomers (M), dibranched isomers (B) and cracking products (C) as functions of the *n*-decane conversion.

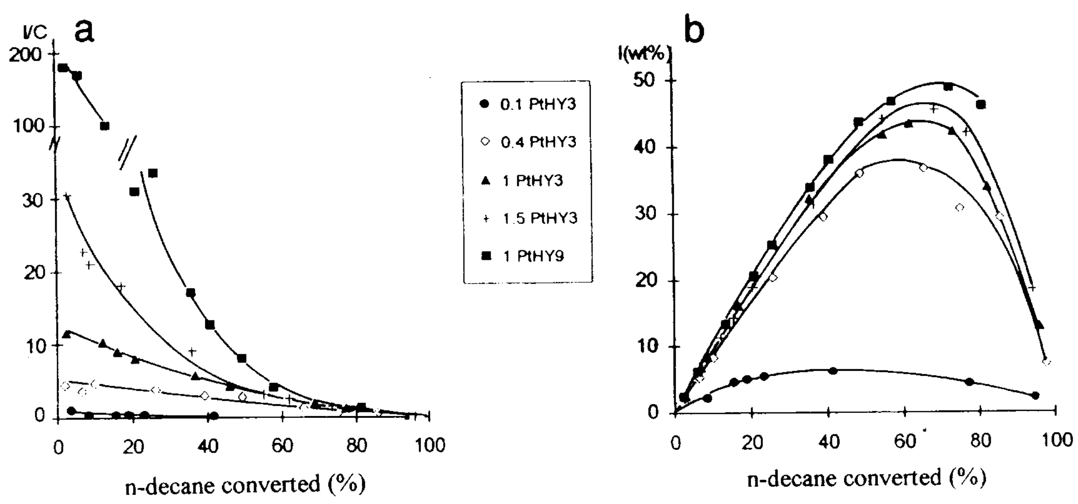


FIG. 4. (a) Ratio of the isomerized/cracked *n*-decane (I/C), and (b) yield of *n*-decane isomers (*I*) as functions of the *n*-decane conversion.

($n_{Pt}/n_A = 0.006$) to 50% for 1 PtHY9 ($n_{Pt}/n_A = 0.17$). The ratio M/B of mono to multibranched isomers decreases when increasing the conversion. The greater the n_{Pt}/n_A value of the catalyst, the greater M/B (Fig. 5).

The distribution of monobranched isomers (Fig. 6) changes with the conversion, approaching that corresponding to thermodynamic equilibrium at high conversion levels on all the catalysts, i.e., 2MC9, 24.4%; 3MC9, 22.7%; 4MC9, 22.7%; 5MC9, 11.5%; 3EC8, 5.3%; 4EC8, 10.5%; 4PC7, 2.9% (19). Whatever the catalyst, all the methylnonanes and ethyloctanes are directly formed from *n*-decane (primary products, Fig. 6a). It is difficult to determine whether propylheptane is an apparent primary product of *n*-decane transformation or a secondary product. However, the rapid initial increase in the selectivity to this isomer (Fig. 6b) could indicate that propylheptane results more probably from a rapid transformation of the other monobranched isomers than from a direct transformation of *n*-decane. The initial distribution depends on n_{Pt}/n_A: the methylnonanes/ethyloctanes ratio increases with n_{Pt}/n_A (Fig. 7a); the percentage of 2MC9 in the methylnonanes mixture decreases when n_{Pt}/n_A increases, while those of the other methylnonanes increase (Fig. 7b); the 4EC8/3EC8 ratio decreases when n_{Pt}/n_A increases (Fig. 7a). The greater the n_{Pt}/n_A value, the greater the differences between the initial and the thermodynamic equilibrium distributions.

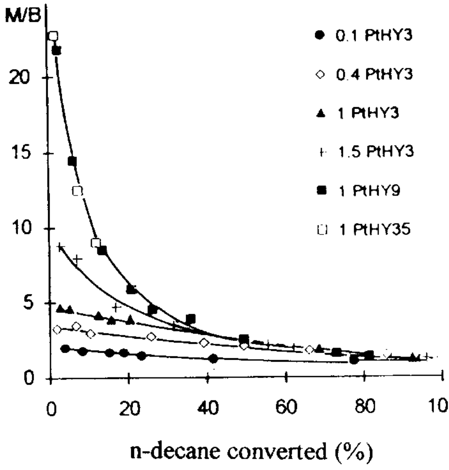
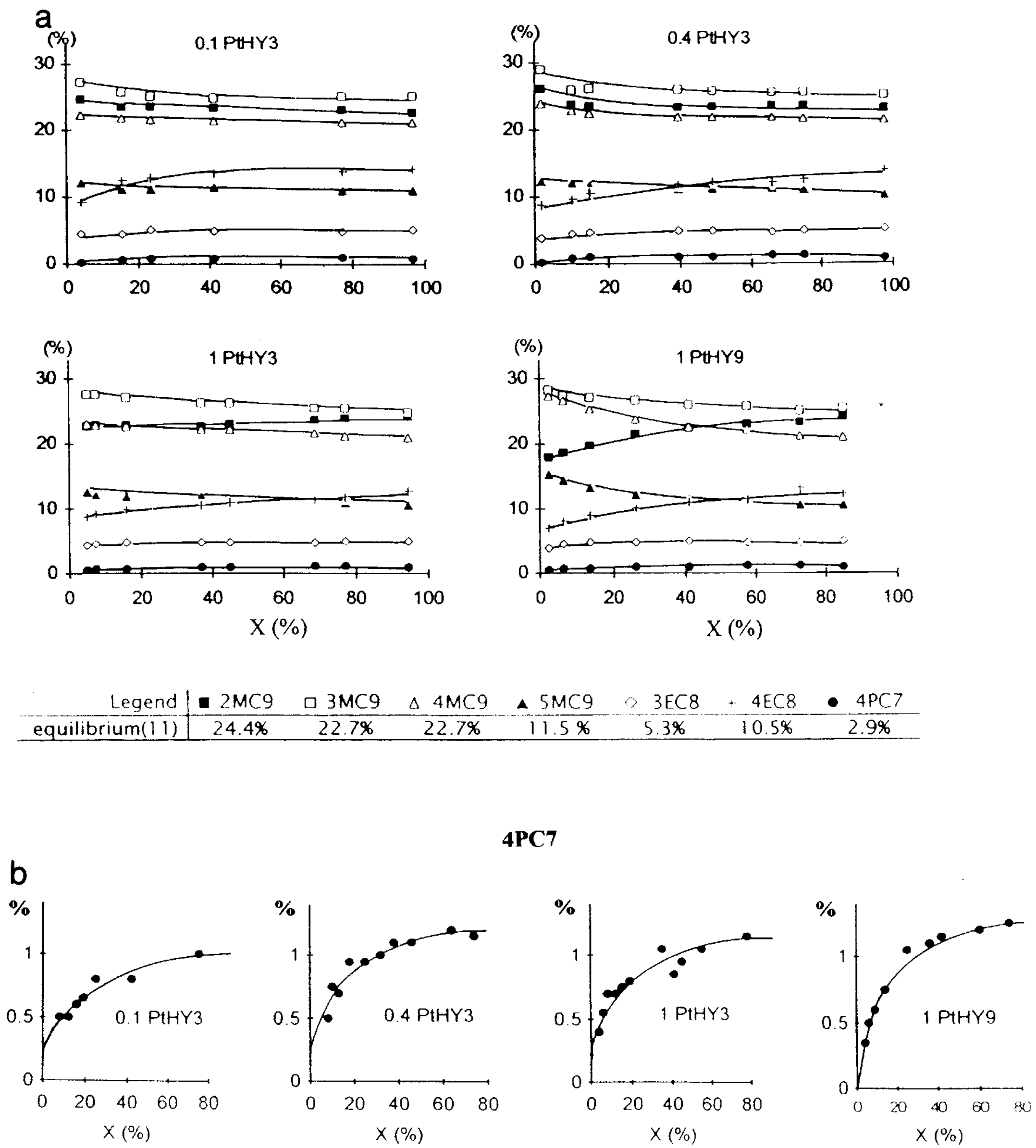


FIG. 5. Monobranched/dibranched isomers ratio (M/B) as a function of the *n*-decane conversion.

The distribution of dibranched isomers is given in Table 2 for total conversions of 20 and 50% and conversions into multibranched isomers between 2 and 12%. Tribranched isomers are formed in low amounts. Thus in the conditions of Table 2 the ratio of the dibranched to the observed tribranched isomers is 10 to 20 times greater than its thermodynamic equilibrium value. The distribution changes little with the catalyst or with the conversion. It is very different from the thermodynamic equilibrium distribution: in particular 2,4- and 3,4-dimethyloctanes are highly favored and 2, 2- and 2, 3-dimethyloctanes are very unfavored (Table 2).

The distribution of cracking products depends little on the catalyst and on the conversion (Table 3). Whatever the catalyst and the conversion, the main cracking products are $C_4 + C_6$ in equimolar amounts (corresponding to 55–60% of the cracking products) and C_5 (30–35%). A low amount of $C_3 + C_7$ hydrocarbons in equimolar amounts is also formed (5–10%). The C_4–C_7 products are mainly branched, the branching increasing with the number of carbon atoms. There is a decrease in the amount of C_3–C_7 with increasing n_{Pt}/n_A and an increase in the branching of the cracking products (Table 3). Moreover, in the C_7 cracking products a small increase of the 2-methylhexane/3-methylhexane ratio is found.



Legend	■ 2MC9	□ 3MC9	△ 4MC9	▲ 5MC9	◇ 3EC8	+ 4EC8	● 4PC7
equilibrium(11)	24.4%	22.7%	22.7%	11.5 %	5.3%	10.5%	2.9%

FIG. 6. Distribution of monobranched isomers (a) and percentage of propylheptane in the monobranched isomers (b) as functions of the *n*-decane conversion (X).

DISCUSSION

As was found with *n*-heptane transformation at 523 K (8, 13, 14) and at 473 K (20), the activity, the stability, and the selectivity of PtHY catalysts for *n*-decane transformation depend significantly on $n_{\mathrm{Pt}}/n_{\mathrm{A}}$, the ratio of the number of hydrogenating to strong acid sites (Table 4). The effect of n_{Pt} at constant n_{A} is shown in the PtHY3 catalyst series.

The introduction of well-dispersed platinum in HY3 has the following consequences:

(i) increase of the initial activity A_0 of the zeolite (×4 at the maximum);

(ii) significant improvement of the stability (A_{f}/A_0 passes from 0.05 with HY3 to 1 for platinum contents equal or greater than 1%);

(iii) significant increase of the selectivity to isomerization I (at the expense of cracking C). At low conversion I/C, close to zero with HY3, is greater than 30 with 1.5 PtHY3.

The change in the number of acid sites at constant n_{Pt} value causes also a significant modification of the catalytic properties. In particular:

— the higher the Si/Al ratio the more reduced the activity of the 1 PtHY samples (Fig. 1);

— the I/C and M/B (monobranched/multibranched isomers) ratios are much higher with PtHY9 and PtHY35 than with PtHY3 catalysts.

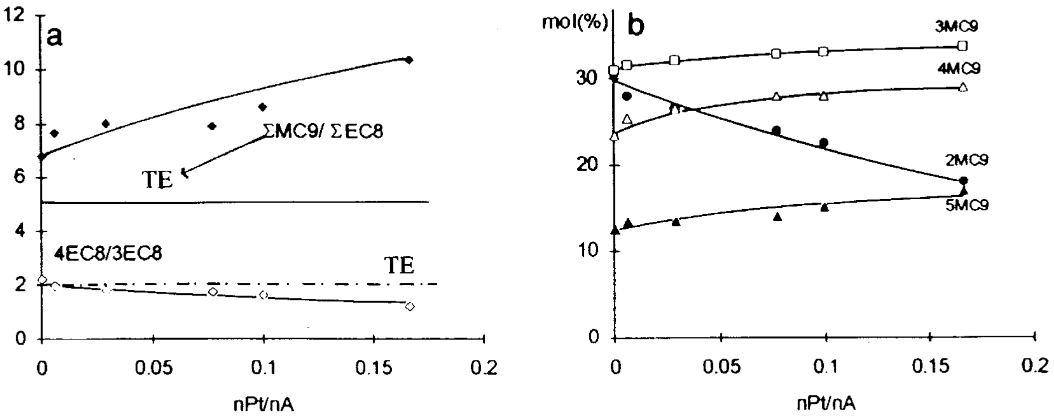


FIG. 7. Initial distribution of monobranched isomers as a function of the ratio of platinum sites/acid sites (n_{Pt}/n_A): (a) 4-ethyloctane/3-ethyloctane and methylnonanes/ethyloctanes ratios; (b) methylnonane distribution. TE: thermodynamic equilibrium.

1. Effect of n_{Pt}/n_A on n-Decane Transformation

The effect of n_{Pt} at constant n_A and of n_A at constant n_{Pt}; hence the effect of n_{Pt}/n_A, on the catalytic properties of the PtHY samples can be explained on the basis of the classical bifunctional mechanism of alkane hydrocracking and hydroisomerization:

(a) dehydrogenation of the alkane on Pt sites,
(b) transport of the alkenes from the Pt sites to the acid sites,
(c) isomerization and cracking of alkenes on the acid sites through carbenium ion intermediates,
(d) transport of the alkenes from the acid to the Pt sites,
(e) hydrogenation of the latter alkenes on the Pt sites.

At low values of n_{Pt}/n_A (<0.03) the Pt sites of PtHY catalysts are not sufficiently numerous for all the acid sites to be fed with intermediate alkenes, which means that the dehydrogenation of the reactant is the limiting step of the alkane transformation. Hence the activity increases proportionally to n_{Pt} for samples having the same n_A value (Fig. 1). The average distance between two platinum sites is great; the number of acid sites which can be encountered by the intermediate alkenes is therefore high, with consequently a high probability of several successive transformations of the alkene before hydrogenation on the acid sites. This explains why dibranched isomers and cracking products appear as primary products (Table 4). Condensation reactions can also occur, finally with the formation of coke molecules. This explains the rapid deactivation of these catalysts.

For PtHY3 catalysts with platinum content equal to or greater than 0.35 wt% (n_{Pt}/n_A > 0.03) the activity increases no more. This means that the Pt sites are sufficiently numerous for all the acid sites to be fed with intermediate alkenes and that the limiting step is the transformation of these alkenes on the acid sites. However, the distance

TABLE 2

Distribution of the Bibranched Isomers

Catalyst	0.1 PtHY3		1 PtHY3		1 PtHY9		Equilibrium value (19)
X_t (%)	20	50	20	50	20	50	
X_B (%)	2	3	4	12	3	12	
2,2DMC8	2.9	2.6	3.0	3.4	2.8	3.5	11.9
2,3DMC8	2.1	1.9	1.7	2.1	2.8	2.7	13.5
2,4DMC8	18.9	22.1	17.4	18.0	18.9	19.8	4.1
2,5DM + 3,5DM + 4,4DMC8	27.8	27.4	30.0	28.8	29.6	28.7	31.1
2,6DMC8	16.7	15.7	16.8	16.3	15.2	15.8	13.7
2,7DM + 3,6DMC8	13.2	11.5	13.0	12.7	10.8	12.1	11.6
3,3DMC8	5.3	7.6	3.9	4.6	6.4	5.1	8.9
3,4DMC8	9.6	8.9	11.2	10.0	11.8	9.4	2.6
4,5DMC8	1.4	0.9	1.1	1.9	1.4	1.4	1.3
MEC7	2.1	1.4	1.9	2.2	3.1	1.5	1.2
Total (moles)	100	100	100	100	100	100	100

Note. X_t, Total conversion; X_B, Conversion into bibranched isomers.

TABLE 3

Distribution of the Cracking Products for 5% Cracking Conversion

Catalyst	0.1 PtHY3	1 PtHY3	1.5 PtHY3	1 PtHY9
n_{Pt}/n_A	0.006	0.077	0.10	0.17
Number of moles/100 *moles cracked*				
$C_3 + C_7$	21	24	25	14
$C_4 + C_6$	112	110	108	117
C_5	67	66	67	69
Total	200	200	200	200
%iso in				
C_4	78	74	75	82
C_5	83	82	82	88
C_6	87	86	87	90
C_7	95	95	95	94

between two platinum sites remains great enough for part of the *n*-alkene molecules to encounter enough acid sites to be transformed successively into monobranched and dibranched isomers (Table 4). Coke molecules are also formed with the consequent deactivation of the catalyst.

With 1 PtHY9 ($n_{Pt}/n_A = 0.17$), 1 PtHY35 ($n_{Pt}/n_A = 0.48$), and 1.5 PtHY3 ($n_{Pt}/n_A = 0.10$) *n*-decane is successively transformed into monobranched isomers M, multibranched isomers B, then into cracking products (Table 4). With these catalysts the number of acid sites encountered by the decene intermediates is such that only one transformation of decenes (branching isomerization or β-scission) can occur before hydrogenation. Therefore these bifunctional catalysts can be considered as ideal: the activity per acid site is maximal (Fig. 1), the formation of coke and the deactivation are very slow (Fig. 2), and the apparent reaction scheme $n\text{-}C_{10} \rightleftharpoons M \rightleftharpoons B \rightarrow C$ is the same as the scheme of transformation of the corresponding olefinic intermediates. However, the M/B ratio is greater with 1 PtHY9 and 1 PtHY35 than with 1.5 PtHY3, which shows that ideality (only one transformation of decene intermediates before hydrogenation) is not achieved with 1.5 PtHY3. Therefore the ideal situation occurs when the number of acid sites which may be encountered by the olefinic intermediates during their diffusion between two metallic sites is lower than 6 ($n_{Pt}/n_A \geq 0.17$). The decrease in the acid site density from PtHY3 to PtHY9 and PtHY35 catalysts can also play a role in the increase of stability (Fig. 2). Indeed, the lower the number of sites of a HY zeolite, the slower the coke formation and the deactivation (21).

For the high values of n_{Pt}/n_A the activities of PtHY3, PtHY9, and PtHY35 catalysts are at their maximum value. These maximal activities should be proportional to the number of active sites. However, as was found in the case of *n*-heptane trnsformation (14), the activity per acid site decreases from PtHY3 (48 h^{-1}) to PtHY9 (10 h^{-1}) and to PtHY35 (1 h^{-1}). This is probably because n_A measured by ammonia adsorption is the sum of protonic sites (which are the active sites) and of Lewis sites (inactive) and that the dealumination increases the ratio Lewis/protonic sites (22). However, other explanations could be proposed: (i) presence of very strong acid sites (superacid sites) on HY3 due to a synergistic effect of extraframework aluminum species on the protonic acid sites (23, 24), (ii) blockage caused by alumina deposits of the access of reactant to some of the pores of HY9 and HY35.

TABLE 4

Hydroisomerization and Hydrocracking of *n*-Decane on PtHY Catalysts

n_{Pt}/n_A	>0.10	>0.03 <0.10	<0.03
Activity	Maximal	Maximal	Low
Stability	Perfect	Average	Low
Reaction scheme	$nC_{10} \rightleftharpoons M \rightleftharpoons B \longrightarrow C$	$nC_{10} \rightleftharpoons (M, B) \longrightarrow C$	$nC_{10} \begin{array}{l} \overset{\rightleftharpoons}{\nearrow} M \\ \rightleftharpoons B \\ \searrow C \end{array}$

Note. Influence of n_{Pt}/n_A on the activity per acid site, on the stability, and on the apparent reaction scheme.

2. Mechanisms of Olefinic Intermediate Transformation

These mechanisms will be discussed on the basis of the product distribution obtained on ideal catalysts, i.e., catalysts for which the olefinic intermediates undergo only a single reaction during their transport between two platinum sites. 1 PtHY9 was preferred to 1 PtHY35, for with this the latter catalyst part of the light products result from hydrogenolysis. With this ideal catalyst the apparent reaction scheme matches the transformation scheme of the olefinic intermediates. This transformation involves as the limiting step the isomerization or the cracking of carbenium ions resulting from olefinic intermediate adsorption on the zeolite protonic sites. Therefore the mechanisms of these carbenium ion transformations and their relative rates could be deduced from the product distribution.

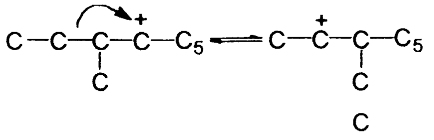
2.1. *Isomerization Reactions*

The isomerization reactions of carbenium ions can be classified into two categories: These are type *A* isomerization, which changes the position of a side chain without changing the degree of branching, and type *B* isomerization, which increases or reduces the degree of branching (25). It is generally assumed that type *A* isomerization occurs through 1,2 alkyl shift and type *B* through protonated cyclopropane (PCP) intermediates. These intermediates allow us to explain the isomerization of *n*-decenes into methylnonenes, that of methylnonenes into dimethyloctenes and that of dimethyloctenes into trimethylheptenes. The initial distribution of methylnonenes (drawn from extrapolation at zero conversion of curves in Fig. 6a is furthermore very close to that expected on a statistical basis from branching of decenes through PCP intermediates (5, 25):

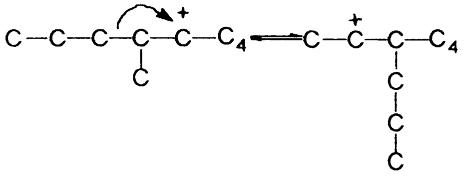
Calculated distribution: 16.7% of 2-methylnonane, 33.3% of 3-methyl and of 4-methylnonanes, 16.7% of 5-methylnonane.

Experimental distribution: 18.3% of 2-methyl, 34.0% of 3-methyl, 30.7% of 4-methyl, and 17.0% of 5-methylnonanes.

However, these PCP intermediates cannot explain the formation of ethyloctanes as primary products. This formation could be explained by an extremely fast rearrangement of methylnonenes through ethyl shift (Scheme 1) or propyl shift (Scheme 2). This explanation seems most unlikely. Indeed, if it was the case, 3- and 4-ethyloctanes which can inter-isomerize through ethyl shift (Scheme 3) would be initially in thermodynamic equilibrium, which is not observed (3EC8/4EC8 = 0.75 initially instead of 0.50 at equilibrium). The primary formation of ethyloctanes can most probably be explained by the participation in *B* isomerization reactions of protonated cyclobutane intermediates (PCB) as proposed by Martens and Jacobs (25) (e.g., Scheme 4). Protonated cyclopentane intermediates were also proposed (25) to explain the formation of 4-propylheptane as a primary product in *n*-decane transformation on Pt/USY and Pt/CaY catalysts. As indicated above, this alkane does not appear on 1 PtHY9 as a primary product. Therefore, the formation of this alkane is most likely to involve the secondary isomerization of 4-ethyloctenes through *n*-propyl shift.



SCHEME 1



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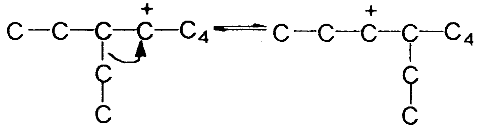

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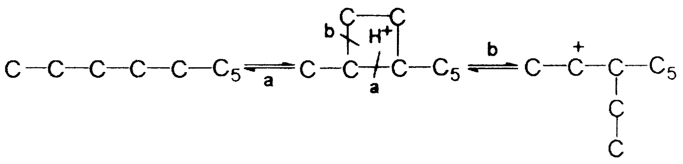


SCHEME 4

Type *A* isomerization is known to be faster than type *B* (25, 26). In decane transformation, the methyl shift would be 70 times faster than branching via protonated cyclopropanes (25). A smaller difference was found with hexanes: inter-isomerization of methylpentanes was found to be about 10 times faster than *n*-hexane branching (26). This difference of one order of magnitude is more likely, since thermodynamic equilibrium between monobranched decane isomers can only be attained at very high conversions (Fig. 6a—1 PtHY9). The comparison between the curves giving as a function of *n*-decane conversion the approach to thermodynamic equilibrium (ATE) for these isomerizations allows us to estimate their relative rates. This is done in Fig. 8 for monobranched isomers in the *n*-decane plus monobranched isomers mixture and for 2-methylnonane in the methylnonanes mixture. From the initial slopes of the curves it can be estimated that *n*-decene isomerization through protonated cycloalkane intermediates is 6–7 times slower than methyl shift in methylnonenes.

2.2. Cracking Reactions

Cracking of monobranched C$_{10}$ alkenes occurs through a type *C* mechanism (which involves two secondary carbenium ion intermediates), that of dibranched C$_{10}$ alkenes through type B_1 or B_2 mechanisms (one secondary plus one tertiary carbenium ion) and type *C* mechanisms and that of tribranched C$_{10}$ alkenes through type *A* (two tertiary

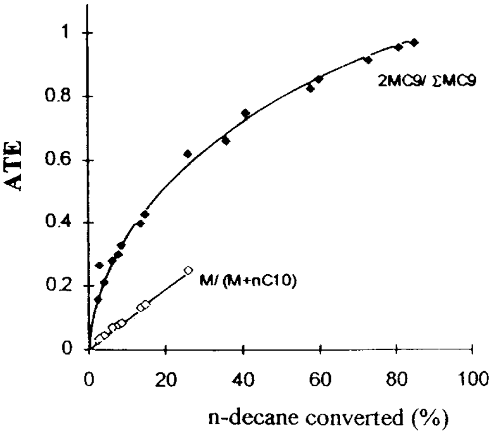
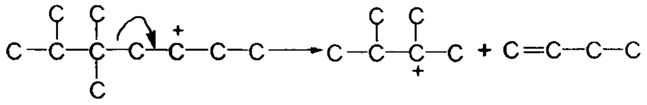


FIG. 8. Approach to thermodynamic equilibrium (ATE) as a function of the *n*-decane conversion on 1 PtHY9 catalyst (ATE = 1 means that thermodynamic equilibrium is achieved).

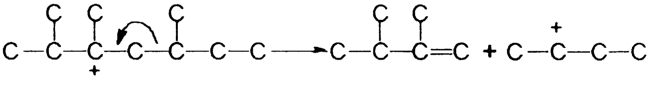
carbenium ions), B_1, B_2, and *C* mechanisms. Reactions which occur through the very unstable primary carbenium ions (such as *n*-decene cracking), are very slow and will not be considered.

On 1 PtHY9 there is no direct formation of C_3-C_7 hydrocarbons from *n*-decane or of monobranched isomers M (Fig. 3). Cracking occurs only from B isomers, i.e., from dibranched and tribranched isomers. The same conclusion was drawn by Martens *et al.* (27) in a detailed investigation of the modes of long-chain alkane hydrocracking on a PtUSHY catalyst. From this observation it can be concluded that type *C* cracking of monobranched alkenes is very slow in comparison with their transformation into branched isomers (type *B* isomerization) and with that of these dibranched alkenes into cracking products. Type *C* cracking is therefore negligible in comparison with types B_1, B_2, and *A* cracking. This can be confirmed by considering the distribution of cracking products. *n*-Heptane which can result only from type *C* cracking (of monobranched or of dibranched isomers) is formed only in very low amounts (at the maximum 0.6 mole for 200 moles of cracking products). The difficulty of *C* cracking compared to the *B* mode of cracking was already shown in *n*-heptane transformation at 473 K (20). Indeed, the cracking products were essentially composed of propane and isobutane in equimolar amounts, *n*-butane which would result from a *C* cracking reaction being formed only as traces (iso/*n*-butane ratio > 100).

The cracking products which can be formed through type *A* cracking of tribanched C_{10} isomers (isobutane, isopentane, 2- and 3-methylpentanes) are greater in amounts than the other ones (propane, *n*-butane, *n*-pentane, *n*-hexane, 2- and 3-methylhexanes). This indicates that most probably *B* ($B_1 + B_2$) cracking of dibranched C_{10} decenes (Bi) is much slower than the isomerization into tribranched decenes (Tri) followed by their cracking through type *A* mechanism. Type *B* cracking of tribranched decenes is, furthermore, negligible in comparison to their A cracking. Indeed, only traces of 2,3-dimethylbutane which would result from B_1 and B_2 cracking of tribranched decenes (Schemes 5 and 6) are observed (at the maximum 0.4 mole for 200 moles of cracking products).



SCHEME 5



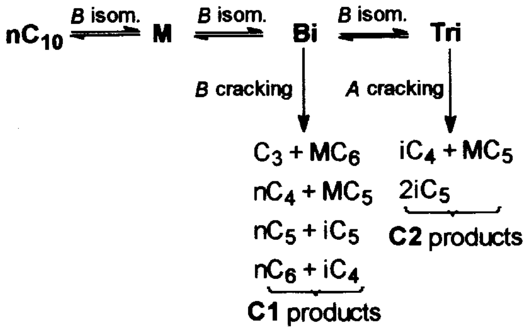
SCHEME 6

It can therefore be concluded that:

(i) type *A* cracking is much faster than type *B* which is itself much faster than type *C* cracking.

(ii) *B* cracking of tribranched isomers (Tri) is negligible in comparison to their *A* cracking while *C* cracking of dibranched isomers (Bi) is negligible in comparison to their *B* cracking.

The reaction scheme of *n*-decane transformation (or *n*-decene transformation) is represented in Scheme 7.



SCHEME 7

The difference between this scheme and the one proposed by Martens *et al.* (25, 27) lies in the origin of the cracking products. Indeed these authors propose the participation of *C* and *B* cracking of dibranched isomers and of *C*, *B*, and *A* cracking of tribranched isomers.

An estimation of the relative rates of *C*, *B*, and *A* cracking can be made from the relative amounts of the corresponding cracking products and decane isomers. Thus for 3% of cracking, 0.02% result from *C* cracking, 0.95% from *B* cracking, and 2.03% from *A* cracking, while the reaction mixture comprises 28.1% of monobranched decanes, 9.45% of dibranched, and 0.45% of tribranched isomers. By assuming a pseudo-first order of reaction it can be deduced that *B* cracking is about 190 times faster than *C* cracking (0.95/9.45)/[0.02/(28.1 + 9.45)], while *A* cracking is 45 times faster than *B* cracking (2.03/0.45)/(0.95/9.45). These calculations, made for all experimental data from 25% *n*-decane conversion to 81.5%, give values of *B*/*C* cracking between 150 and 280 and of *A*/*B* cracking between 35 and 55.

A kinetic model has been developed for *n*-alkane hydroisomerization and hydrocracking on bifunctional ideal catalysts (28, 29). With this kinetic model all the steps of the reaction scheme can be considered as pseudo-first order with respect to the reactants. The relative rate constants were determined by comparing the experimental data to calculated curves, giving the yields in each type of products as a function of the *n*-decane conversion. For this estimation of the rate constants it was supposed that monobranched C_{10} isomers as well as dibranched (Bi) and tribranched isomers (Tri) were formed in their thermodynamic equilibrium

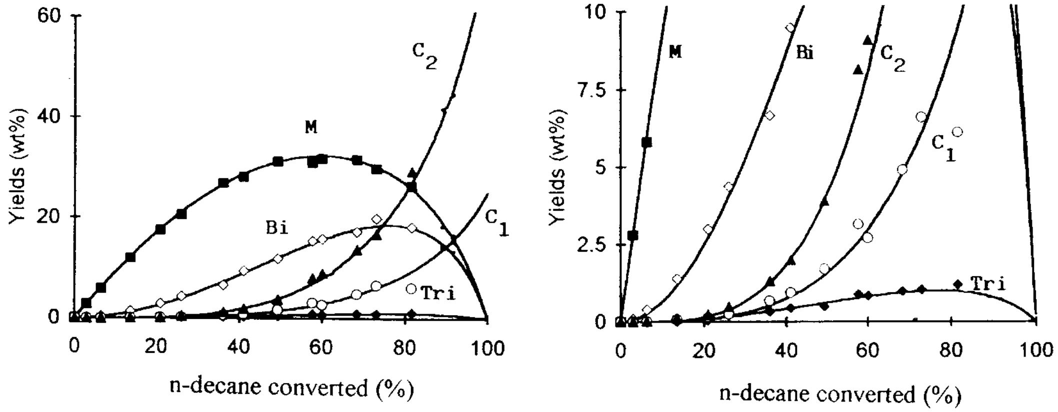


FIG. 9. Yields (wt%) of products of *n*-decane hydroisomerization and hydrocracking versus *n*-decane conversion (wt%). Calculated curves (with the rate constants of Table 5) and experimetnal points: *n*-C_{10}, *n*-decane; M, monobranched iosmers; Bi, dibranched isomers; Tri, tribranched isomers; C_1, products of Bi cracking; C_2, products of Tri cracking.

mixture. Figure 9 shows that a good agreement is obtained for the set of relative rate constants given in Table 5 (a value of 10 was attributed to the transformation of *n*-decane into M). It can be noted that the branching of *n*-decane, that of M and that of Bi occur at similar rates. On the other hand, in agreement with the previous calculations, the cracking of tribranched isomers is about 50 times faster than the cracking of dibranched isomers.

CONCLUSION

In this paper we report a quantitative relationship between the activity, the stability, and the selectivity for *n*-decane hydroisomerization and hydrocracking on bifunctional PtHY catalysts and the ratio of the number of metallic sites to the number of acid sites. In particular, as shown previously with *n*-heptane hydrocracking (8, 12, 13), the apparent reaction scheme depends on the number of acid sites which may be encountered by the olefinic intermediates during their diffusion between two metallic sites. For a large number of acid sites *n*-decane leads directly to all the isomerization and cracking products. For a number of acid sites below 6, *n*-decane transforms successively into monobranched isomers, dibranched isomers plus cracking products. In this latter situation the catalysts can be considered as **ideal bifunctional catalysts** since there is neither limitation by the hydrogenation and dehydrogenation steps nor by the migration of olefinic intermediates between hydrogenating sites. Therefore the activity per acid site is maximal and the apparent reaction scheme matches the transformation scheme of olefinic intermediates.

Information on the mechanisms of cracking and isomerization of olefinic intermediates on the acid sites can be obtained from the product distribution established on these ideal catalysts. Thus it has been shown that:

(i) the cracking products result from β-scission either of dibranched decenes through mode *B* (which involves one tertiary and one secondary carbenium ion intermediates), or of tribranched decenes through mode *A* (two tertiary carbenium ion intermediates): the β-scission through mode *C* (two secondary carbenium ion intermediates) can be neglected.

(ii) branching of *n*-decenes occurs mainly through protonated cyclopropane intermediates (PCP) and for a small part through protonated cyclobutanes (PCB),

(iii) the various steps of cracking and isomerization can be classified in the following order as a function of their rates:

$$A \text{ cracking} > A \text{ isomerization} > B \text{ isomerization} > B \text{ cracking} \gg C \text{ cracking}.$$

Type *A* cracking is about 4 times faster than *A* isomerization (through methyl shift), 20 times faster than *B* isomerization (through PCP intermediates), 50 times faster than *B* cracking, and 10,000 times faster than *C* cracking.

TABLE 5

Relative Rate Constants of Hydroisomerization and Hydrocracking of Decane Isomers on 1 PtHY9

Operating conditions: T = 473 K, $p_{H_2} = 0.9$ bar, $p_{n\text{-decane}} = 0.1$ bar
Reference: $k_{n\text{-}C_{10}\rightarrow M} = 10$

$$\begin{tikzcd}
nC_{10} \arrow[r, shift left, "10"] & M \arrow[l, shift left, "1.25"] \arrow[r, shift left, "13.8"] & Bi \arrow[l, shift left, "5.6"] \arrow[r, shift left, "13.2"] \arrow[d, "4"] & Tri \arrow[l, shift left, "25.3"] \arrow[d, "220"] \\
 & & C_1 & C_2
\end{tikzcd}$$

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