

Carbon-14 Tracer Study of the Conversion of Labeled *n*-Propylcyclopentane during *n*-Octane Aromatization with a Pt–Zeolite L Catalyst

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n-Propylene cyclopentane or *n*-propylcyclopentane labeled in the ring with ^{14}C was converted together with *n*-octane using a Pt–KL zeolite catalyst operating at 482°C and ca. 14 bar. The products indicate that hydrogenolysis to produce isooctanes, not ring expansion to produce aromatics, is the major reaction pathway for the alkyl cyclopentane compound. Dilution of the ^{14}C activity in *n*-propylcyclopentane during the conversion shows that C_5 as well as C_6 cyclization occurs during the conversion of *n*-octane. The current data were obtained with a catalyst that has a Pt crystal size range that is similar to those reported earlier. Furthermore, the conversion data for *n*-octane and *n*-propylcyclopentane using the Pt–KL zeolite catalyst are very similar to data obtained with catalysts based on other nonacidic supports where the Pt crystals cannot be located in a zeolite type channel. Thus, for *n*-octane conversion, it appears that the Pt in L zeolite catalysts has selectivities that are similar to Pt on other nonacidic supports. © 1992 Academic Press, Inc.

INTRODUCTION

Alkane conversion to aromatics has proven to be more complex than many early investigators realized (1). The early name for this reaction—dehydrocyclization (implying dehydrogenation followed by cyclization) or cyclodehydrogenation (implying cyclization followed by dehydrogenation)—illustrates a point of debate that is not fully resolved even today. With the improved analytical procedures developed since the reaction was discovered in the 1930's, results have been obtained that produced disagreement over the cyclization step: Was the primary cyclic product, irrespective of the detailed mechanism, a five-carbon, a six-carbon, or another sized ring? Goetschel and Pines (2), on the basis of ^{14}C tracer studies, concluded that all possible ring sizes were formed and, furthermore, the relative contributions of each ring size could vary with catalyst age as well as depend upon the catalyst or even the catalyst

support. In this mechanism, the intermediates for *n*-octane dehydrocyclization could include all ring sizes from cyclopropane to cyclooctane; ring expansion and/or contraction as a secondary reaction leads to aromatics. Kazanskii *et al.* (3, 4) also emphasized the dependence of ring size of the primary product upon the catalyst; he appeared to favor the view of five carbon ring formation with metals and six-carbon ring formation with oxide catalysts (5). Gault and co-workers ((6) for example) found evidence for direct six-carbon ring formation but also indicated that mechanisms involving other size rings were involved. Others (7) proposed that at least 80% of the aromatics formed could be accounted for by direct six-carbon ring formation for all catalysts; furthermore, isomerization during or prior to cyclization could account for the minor products.

The above results were, for the most part, obtained at 1 bar pressure, or lower, while naphtha reforming is carried out in the 3.5- to 26-bar range. There have been far fewer

mechanistic studies at these more relevant pressures. Callender *et al.* (8), among others, advance the view that, under typical reforming conditions, cyclization by the platinum function occurs principally by five-carbon ring formation followed by ring expansion. Csicsery and Burnett (10) obtained data to show that isomerization probably proceeded, at 18.6 bar with a Pt-SiO₂ catalyst, through a five-carbon ring intermediate followed by hydrogenolysis; direct aromatization was not a major reaction pathway for a five number ring intermediate. The aromatics formed at 13.8 bar over Pt- and Pt-Sn-alumina catalysts were consistent with direct six-carbon ring formation (7, 9, 11).

Davis (12) proposed that two cyclization pathways operate but only one leads to aromatics. Hardy and Davis (13) found that aromatics are formed more rapidly from the *n*-alkane than from a C₈ alkylcyclopentane. These latter authors concluded that at higher pressures typical of naphtha reforming the data did support a metal-catalyzed cyclization mechanism that included the formation of both five- and six-carbon ring intermediates; however, the five-carbon rings led primarily to isoalkanes and not aromatics.

The introduction of the Pt-KL zeolite catalysts has raised further issues. Ever since metal-loaded zeolites have been used, there has been a debate about whether the metal is located on the exterior or within the zeolite. This issue has become an especially important point with Pt-KL zeolite catalysts since mechanisms have been proposed that suggest pore geometry determines the catalyst selectivity. Even the zeolite crystal size has been introduced as a factor that determines activity and catalyst life (17, 18).

Derouane and Vanderveken (19) considered the aromatization of *n*-hexane on Pt-L zeolite catalysts. They introduce the idea that adsorbates tend to optimize their van der Waals interaction (20) and that this may lead to preorganization. They propose four steps for *n*-hexane conversion to benzene

that include diffusion of *n*-hexane through the channel to meet Pt, atom, or crystal, head on so that interaction is with a terminal methyl group and then a C₁-C₆ metallocycle is formed and this species acts as the precursor to cyclohexane, cyclohexene, and eventually benzene.

Derouane and Vanderveken (19) consider that structural recognition and preorganization appear as central determinants to the direct 1,6-ring closure. Complimentarity of the chain length and of the size and shape of the zeolite cage dominates in preorganization. Chain lengths longer than C₆ or branching should congest and destabilize the molecules (guest)-zeolite (host) complex to various degrees and thus decrease catalytic activity, as observed. Chevron workers, however, report similar relative conversions (within 30%) for *n*-hexane and *n*-nonane.

Besoukhanova *et al.* (21) characterized a 5 wt% Pt-KL zeolite catalyst and used a 0.6 wt% Pt-KL catalyst for *n*-hexane dehydrocyclization, presumably at about atmospheric pressure. These authors concluded that: (1) the basic environment of the zeolite generates sites on Pt different from other supports, e.g., Y zeolite, and these sites are selective for producing aromatics from *n*-hexane, and (2) the 10- to 25-Å Pt crystals filling the zeolite pores are concerned with catalysis and their activity is strongly dependent upon their basic environment.

Tauster and Steger (22) also presented a model that explicitly involves the zeolite nature of the carrier. A plot of the selectivity of hexane aromatization versus terminal cracking (e.g., pentanes/butanes) shows that selective aromatization catalysts are also selective for terminal hydrogenolysis (reproduced in Fig. 13). The majority of the data were collected 3-4 h after introduction of *n*-hexane feed although additional data were given for samples collected after 23-26 h on feed. For Pt-SiO₂, where the data must be for the selectivity of out-of-channel Pt, the data represent an extreme from that of a selective Pt-KL zeolite catalyst. Other

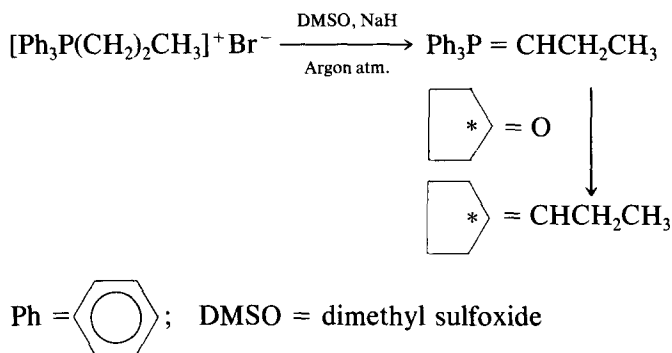
Exxon workers (23) have produced catalysts with selectivities similar to Pt-KL from Pt containing dealuminated faujasites (Si/Al₂ ~40). Tauster and Steger therefore conclude that the unique properties of Pt-KL cannot be due to either its high potassium content (e.g., basicity) or to details of its zeolite channel structure. These authors contend that cavities (zeolite L) or supercages (faujasites) that contain Pt are the reaction sites. The fact that the Pt clusters in the cavities/supercages are accessible only through portholes of ~7.3 Å in KL has a profound effect on their catalytic properties. The channel size dictates that molecules longer than butane must transverse through the 7.3-Å orifice lengthwise, and this will lead to an end-on attachment of the paraffin with the metal surface. This specific catalysis has been termed "molecular die catalysis" by Tauster and Steger.

In view of the debate of the reaction pathway leading to aromatics formation for a Pt catalyst, we have conducted experiments in which a ¹⁴C-labeled alkylcyclopentane was added to the same carbon number *n*-alkane. Thus, *n*-propylcyclopentane, one of the two alkylcyclopentanes that result from a direct five-carbon ring formation from *n*-octane, was converted together with *n*-octane. The catalyst utilized in this study was Pt-L, zeolite which has been reported to be nonacidic and to catalyze aromatization using only the catalytic properties of the platinum clusters (14-16).

EXPERIMENTAL

1. Synthesis and Purification of ¹⁴C-Labeled *n*-Propylene Cyclopentane

¹⁴C-labeled *n*-propylene cyclopentane was synthesized using the following reaction sequences (* indicates ¹⁴C):



The *n*-propylene cyclopentane was purified using adsorption chromatograph. The synthesis mixture was adsorbed on a column packed with silica, which had been calcined at 550°C. 2-Propanol was used as eluent under ca. 1.5 bar nitrogen pressure. The olefin eluted first and was collected. The *n*-propylene cyclopentane was further purified by vacuum distillation to remove residual ether and 2-propanol. The purified *n*-propylene cyclopentane contains ca. 2 mole% ether and 2-propanol. A 3% *n*-propylene cyclopentane solution was prepared

by adding the appropriate amount of the purified *n*-propylene cyclopentane to unlabeled *n*-octane (Fisher, 99+%).

2. Catalyst Preparation

The catalyst was prepared by ion exchange of a sample of the potassium form of Zeolite L. To effect exchange without introducing acidity, the exchange utilized Pt(NH₃)₄Cl₂ as the platinum source. Sufficient Pt complex and about 1.3 mole of KNO₃/mole Pt were added to ca. 50 ml of deionized water to produce ca. 30 g of ex-

changed Zeolite L that contains 0.6 wt% Pt. The zeolite was stirred in this solution for 3 days then collected by filtration and washed on the filter cake with ca. 50 ml water. The ion-exchanged zeolite was dried at 120°C and calcined in air for 4 h at 500°C.

3. Catalytic Reaction

Two catalytic runs were performed. Run 1 was carried out at low severity to define the fate of the ^{14}C -labeled *n*-propylene cyclopentane. Run 2 utilized the products from Run 1 as feed and was at a higher severity in order to follow the conversion of the *n*-propylcyclopentane. For Run 1, 3.0 g of 0.6 wt% Pt/Zeolite L was mixed with 9.0 g α -alumina and for Run 2, 5.2 g 0.6 wt% Pt/Zeolite L was mixed with 5.3 g α -alumina. The catalyst was reduced overnight in a plug flow reactor under 13.8 bar hydrogen at 482°C. At the end of the reduction period, pure *n*-octane was introduced at a rate of 4–5 cc/g-cat/h for Run 1 and 1.3–1.5 cc/g-cat/h for Run 2. *n*-Octane conversion was monitored during the run. For Run 2, after 24–26 h of converting pure *n*-octane, the *n*-octane feed containing the ^{14}C compound was introduced. Following the addition of the ^{14}C -labeled material, pure *n*-octane was again used as a feed for another few hours to evaluate the extent of catalyst deactivation during the conversion of the ^{14}C -containing feed. Liquid product was collected hourly and analyzed using a HP 5880A GC equipped with a 60-ft DB-5 capillary column (J & W). Since the small amount of sample utilized for the capillary GC analysis does not provide sufficient counts for proportional counting in series with the GC, ^{14}C -labeled products were analyzed separately using a HP 5720A GC equipped with a 6-ft packed Bentone-34/diisodecyl phthalate column (Supelco) in series with a Packard Model 894 or a Radiomatic Model GCR gas proportional counter.

RESULTS

n-Octane conversion initially decreased with time during Run 1 and then stabilized

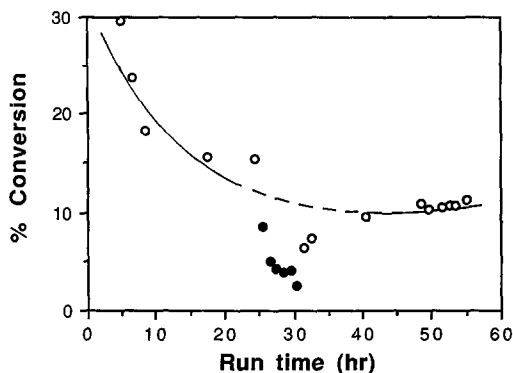


FIG. 1. Conversion of pure *n*-octane (○) and *n*-octane containing 3 wt% *n*-propylene cyclopentane (●) at 13.8 bar (200 psig), 482°C and $\text{H}_2/\text{hydrocarbon} = \text{ca. } 9$.

to a constant value during the latter part of the operation (40–57 h, Fig. 1). When the feed was switched to the 3.0% *n*-propylene cyclopentane/*n*-octane mixture at 24.5 h, a sharp decrease in *n*-octane conversion was observed. A gradual recovery of *n*-octane conversion was observed during the period following the *n*-propylene cyclopentane/*n*-octane conversion (after 31.5 h). The drastic decrease in *n*-octane conversion is most likely due to the presence of *n*-propylene cyclopentane. The *n*-octane conversion following termination of the *n*-propylene cyclopentane-containing feed increases so that the activity at 55 h of use is in line with that anticipated had *n*-octane been the only feed during the total time.

Typical GC and PC chromatograms for the liquid product from the catalytic conversion of the feed containing ^{14}C -labeled *n*-propylene cyclopentane are shown in Fig. 2. The analytical results and the ^{14}C activity distribution for the product obtained during the 25.5- to 33.5-h period are given in Table 1. *n*-Propylene cyclopentane was converted mainly to *n*-propylcyclopentane (>90%). A small quantity of ^{14}C -labeled ethylbenzene was formed as indicated by the small peak in the PC chromatogram. The data clearly eliminate the operation of acid catalysis normally encountered in reforming with bifunc-

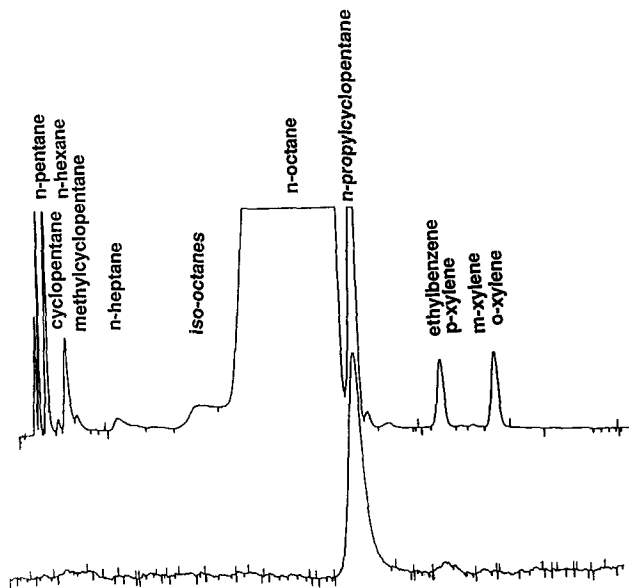


FIG. 2. Liquid product gas chromatograph using a Bentone-34/diisodecyl phthalate column (top trace) and the corresponding proportional counter output (bottom trace) for the conversion of *n*-octane containing 3 wt% *n*-propylene cyclopentane during Run 1 (see text for reaction conditions).

tional catalysts since other C_8 aromatics were not obtained.

Since catalytic hydrogenation of the alkene is the major reaction at low conversion of *n*-octane, the product collected from a 25.5- to 33.5-h period was blended and used

TABLE I

Products from the Conversion of *n*-Octane Containing 3 wt% ^{14}C -Labeled Propylene Cyclopentane with Pt-Zeolite L Catalyst at 482°C and 13.8 bar (Hydrocarbon : H_2 = ca. 1 : 8)

Compound	Wt%	% Radioactivity ^a
<i>n</i> -Pentane	0.47	
<i>n</i> -Hexane	0.40	
<i>n</i> -Heptane	0.17	
Isooctanes	1.61	
<i>n</i> -Octane	92.77	
<i>n</i> -Propylcyclopentane	2.35	95.5
Ethylbenzene	0.51	4.5
<i>o</i> -Xylene	0.59	
Others	1.13	

^a The radioactivity of the other compounds listed in the table is so low that it could not be detected.

as the feed during a period of Run 2 to define the reaction pathway of *n*-propylcyclopentane during *n*-octane conversion.

The conversion of *n*-octane again declines with time-on-stream during Run 2 to approach a constant activity (Fig. 3). Note that the feed was switched from pure *n*-octane at 8 h to *n*-octane containing unlabeled *n*-propylcyclopentane and at 25.5 h to the ^{14}C -containing product obtained from Run 1, re-

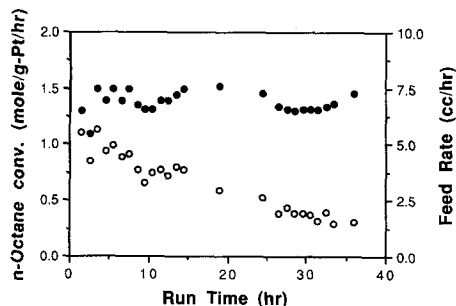


FIG. 3. *n*-Octane conversion (○) and flow rate (●) during Run 2 (see Experimental Section for reaction conditions).

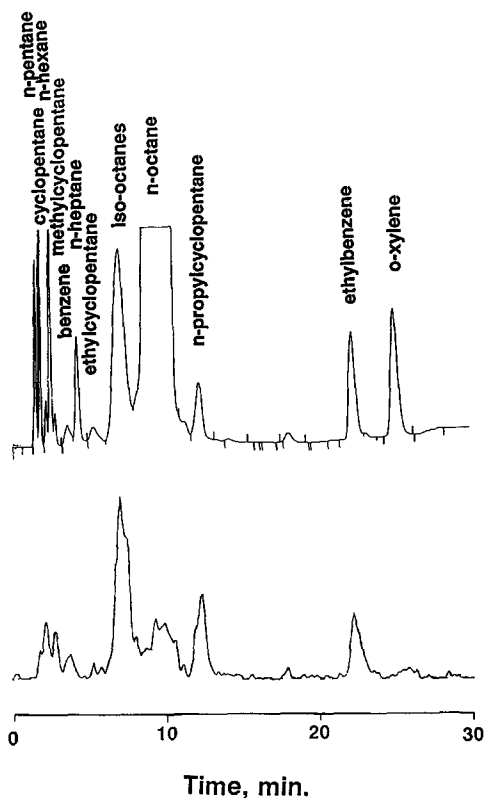


FIG. 4. Liquid product gas chromatograph (top trace) and corresponding proportional counter (bottom trace) for the products from the conversion of *n*-octane during ^{14}C -labeled *n*-propylcyclopentane during Run 2.

spectively. This indicates that the change in the feed to include *n*-propylcyclopentane did not affect catalyst activity as was the case for *n*-propylene cyclopentane.

Typical GC and PC chromatograms for the product from Run 2 collected between 25.5 and 33.5 h are shown in Fig. 4. It can be seen from the PC chromatogram that radioactivity is present in five of the peaks or grouping of peaks. The first group of compounds shown in Fig. 5 that contains ^{14}C includes cyclopentane and methylcyclopentane; the percentage of ^{14}C in this first grouping decreases as the conversion of *n*-propylcyclopentane decreases. The next group containing ^{14}C consists of the methylheptane isomers; the column did not effect separation of 2-, 3-, and 4-methylheptanes and

3-ethylhexane. The next grouping of ^{14}C compounds is that of *n*-octane. The reactant, *n*-propylcyclopentane, is the compound responsible for the fourth grouping containing ^{14}C . The fifth grouping containing ^{14}C is due to ethylbenzene; the three xylene isomers do not contain a detectable amount of ^{14}C . The product distributions of the five groups, based upon ^{14}C distributions, are listed in Table 2 and are plotted as a function of time in Fig. 5. The fraction of *n*-propylcyclopentane (open squares) increases with reaction time, and the fraction of ethylbenzene (open circles) is essentially constant with time. The percentages of the aliphatic C_8 isooctanes (solid circles) and *n*-octane (solid squares) decrease with time. The hydrogenolysis products, methylcyclopentane plus cyclopentane (open circles), decrease slightly with time. This indicates that the selectivity for *n*-propylcyclopentane conversion was changing with time, and this is primarily due to a decrease in the rate for hydrogenolysis of *n*-propylcyclopentane to produce iso- and *n*-octane.

During both periods of Run 2 when *n*-propylcyclopentane was present the ratios of the conversion of the two reactants (open squares) were essentially the same (Fig. 6) even though the total conversion of *n*-octane

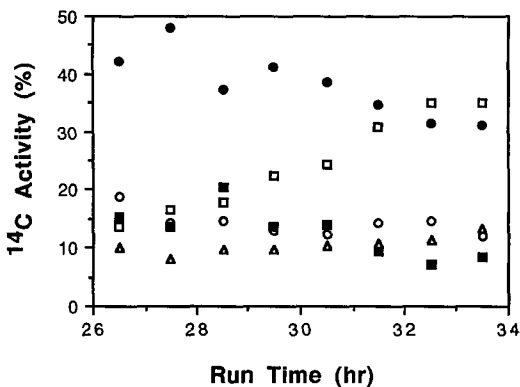


FIG. 5. The percentage of ^{14}C activity present in *n*-propylcyclopentane (□), isooctanes (●), *n*-octane (■), ethylbenzene (△), and methylcyclopentane plus cyclopentane (○).

TABLE 2

Distribution of Radioactivity in Compounds or Groups of Compounds for the Conversion of 3 wt% ^{14}C -Labeled *n*-Propylcyclopentane (Containing 4.5% ^{14}C -Labeled Ethylbenzene) with Pt-Zeolite L Catalyst at 482°C and 13.8 bar (Hydrocarbon : H_2 = ca. 1 : 8)

Time (h)	% Cyclopentane, hexanes, and methylcyclopentane	% Isooctanes	% <i>n</i> -Octane	% <i>n</i> -Propylcyclopentane	% Ethylbenzene
26.5	18.9	42.1	15.2	13.7	10.0
27.5	14.2	47.9	13.5	16.4	8.0
28.5	14.6	37.4	20.3	17.8	9.7
29.5	12.9	41.3	13.5	22.4	9.9
30.5	12.4	38.7	14.0	24.4	10.5
31.5	14.2	34.8	9.5	30.7	10.8
32.5	14.6	31.6	7.0	35.2	11.5
33.5	11.9	31.2	8.5	35.1	13.3

during the second period was only about half of that of the first period.

During the course of the nearly 40-h run the composition of the aromatics varied slightly (Fig. 7). Initially significant amounts of the isomers not allowed by direct six-carbon ring formation, *m*- and *p*-xylene, were formed. The amount of these latter two C_8 aromatics decrease with time. At least a significant fraction of *m*- and *p*-xylene at the higher conversions is due to cyclization of the isooctane isomers produced as primary products. As observed with a Pt on non-acidic alumina catalyst (11) about equal

amounts of ethylbenzene and *o*-xylene are formed.

Hydrogenolysis of alkyl aromatics can occur under reforming conditions, and this was the case in the present study. It is observed that the fraction of aromatics derived from hydrogenolysis—benzene and toluene—decrease with reaction time (Fig. 8). The fraction of *m*- plus *p*-xylene decreases with reaction time and parallels the decline in activity for hydrogenolysis of aromatics. In addition, these two measures of hydrogenolysis activity decline in parallel with the total conversion of *n*-octane (Fig. 8). The

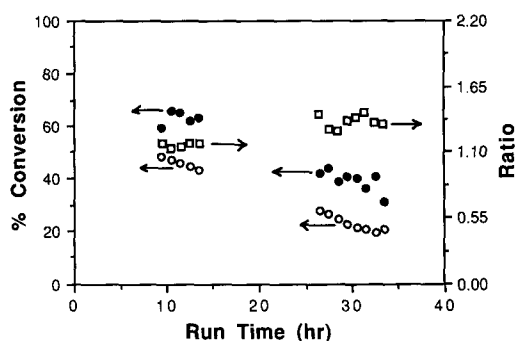


FIG. 6. The percentage conversion of *n*-octane (○) and *n*-propylcyclopentane (●) as well as the ratio of conversion of *n*-propylcyclopentane/*n*-octane (□) during periods of the conversion of a mixture of *n*-octane and unlabeled *n*-propylcyclopentane (8–14 h) and ^{14}C -labeled *n*-propylcyclopentane (26.5–33.5 h).

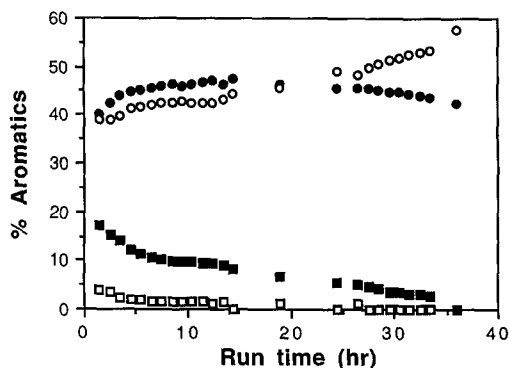


FIG. 7. Composition of the C_8 aromatics during the conversion of *n*-octane or a mixture of *n*-octane and *n*-propylcyclopentane during Run 2: ethylbenzene, (●); *o*-xylene, (○); *m*-xylene, (■); and *p*-xylene, (□).

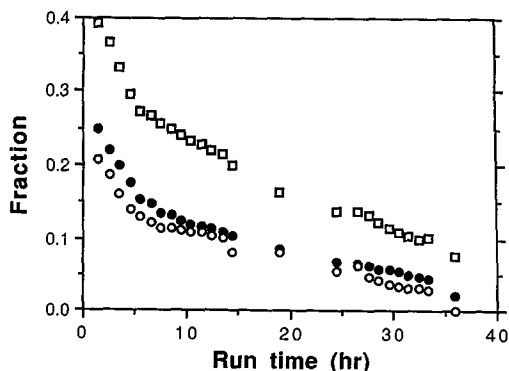


FIG. 8. Fraction of hydrogenolysis of C_8 aromatics [(benzene + toluene)/(total aromatics) (●)], fraction of C_8 aromatics derived from *n*-propylcyclopentane hydrogenolysis [(*m*- + *p*-xylene)/(C_8 aromatics) (○)] and fraction of *n*-octane conversion/2 (□) during Run 2.

similar trend for all three activities—*n*-octane conversion, alkylcyclopentane hydrogenolysis, and C_8 aromatics hydrogenolysis—implies that the three reactions depend upon a common set of catalytic sites.

The production of isoalkanes relative to the aromatics varies with reaction time (Fig. 9). Initially, the total amount of aromatics is nearly twice that of the isoalkanes. With reaction time this ratio changes so that the total isoalkanes produced is about the same as that of the total aromatics at later reaction times. This is not unexpected since, at high C_8 conversions, the primary isoalkane prod-

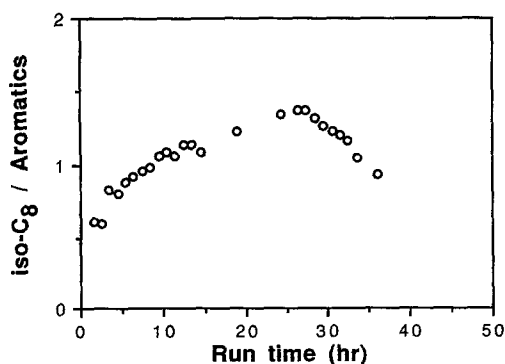


FIG. 9. The ratio of isoalkanes (iso- C_8) and C_8 aromatics products during Run 2.

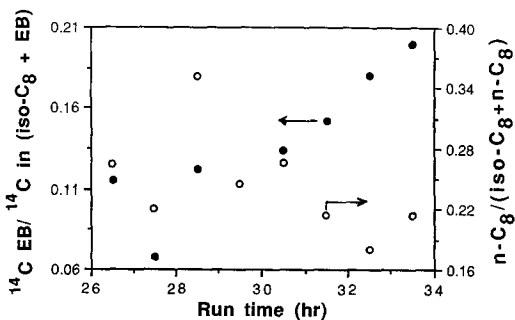


FIG. 10. The fraction of ^{14}C in ethylbenzene (corrected for the 4.5% present in the feed for Run 2) [(% ^{14}C in ethylbenzene-4.5)/(% ^{14}C in isooctanes + ethylbenzene-4.5)] (●) and the fraction of *n*-octane in the C_8 acyclic compounds (○) in the products from Run 2.

ucts will be converted to a greater extent through secondary reactions.

The amounts of ethylbenzene produced from *n*-propylcyclopentane relative to *n*- and isooctanes are shown in Fig. 10. Initially, ethylbenzene (solid circles) comprises only about 10% of the ethylbenzene plus C_8 aliphatics; this fraction appears to increase with reaction time. *n*-Octane (open circles) comprises about 25% of the *n*-iso C_8 -alkane fraction initially and this fraction appears to decrease slightly with conversion. Table 3 shows the ratio of the area of the proportional counter and the corresponding chromatographic peak (PC/GC ratio) for *n*-propylcyclopentane and ethylbenzene. The ratios for both compounds increase with time. Also shown in Table 3 is the PC/GC ratio relative to that of *n*-propylcyclopentane (R_t/R_f) in the feed. The R_t/R_f is an indication of the ^{14}C activity in the compound. Figure 11 shows the R_t/R_f for *n*-propylcyclopentane and ethylbenzene as a function of run time. It can be seen that the increase in the ^{14}C fraction in ethylbenzene during the 6 h when labeled *n*-propylcyclopentane was added is paralleled by an increase in the ^{14}C activity of the *n*-propylcyclopentane in the liquid products of Run 2. Thus, during this 6-h period, the apparent change in selectivity for producing ethyl-

TABLE 3

The ^{14}C Activity of *n*-Propylcyclopentane and Ethylbenzene in Feed and Liquid Products from Run 2

Run time (h)	<i>n</i> -Propylcyclopentane		Ethylbenzene	
	Ratio (R_i) ^a	R_i/R_f ^b	Ratio (R_i) ^a	R_i/R_f , pcp ^c
Feed	0.046	—	0.0093	—
26.5	0.0049	0.10	0.0015	0.032
27.5	0.0087	0.19	0.0017	0.036
28.5	0.010	0.20	0.0029	0.064
29.5	0.0092	0.20	0.0022	0.047
30.5	0.012	0.27	0.0035	0.076
31.5	0.016	0.34	0.0036	0.078
32.5	0.017	0.37	0.0046	0.099
33.5	0.012	0.27	0.0046	0.10

^a Ratio of the areas of the proportional counter and the corresponding gas chromatographic peak.^b R_i for the *n*-propylcyclopentane in the indicated liquid sample divided by the ratio for *n*-propylcyclopentane in the feed.^c R_i for ethylbenzene (corrected for the activity of ethylbenzene in the feed) divided by R_i for *n*-propylcyclopentane in the feed.

benzene relative to isooctanes is due to the decreased dilution of the added ^{14}C -labeled *n*-propylcyclopentane by unlabeled *n*-propylcyclopentane formed from unlabeled *n*-octane. Figure 12 shows the percentage of *n*-propylcyclopentane (open circles) and 1-ethyl-2-methylcyclopentane (solid circles), as well as the ratio of *cis-trans*-1-ethyl-2-methylcyclopentane (open squares), in the liquid products as a function of run time. Following Hour 20 the percentage of 1-

ethyl-2-methylcyclopentane in the liquid products shows a steady decrease. The addition of ^{14}C -labeled *n*-propylcyclopentane causes the percentage of this component to increase slightly, but this is due to a decrease in catalytic activity. The *cis/trans* ratios of the 1-ethyl-2-methylcyclopentane isomers remain constant throughout the entire run.

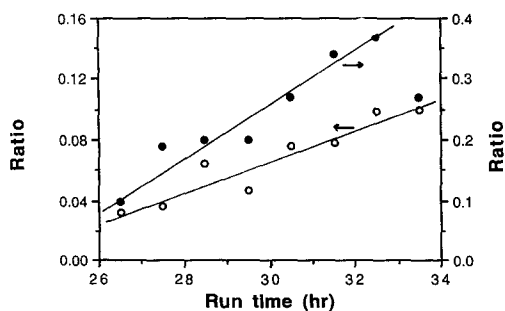


FIG. 11. Ratios of the ^{14}C activity/mole of ethylbenzene (●) or *n*-propylcyclopentane (○) in the products from Run 2 relative to the ^{14}C activity/mole of the feed to Run 2.

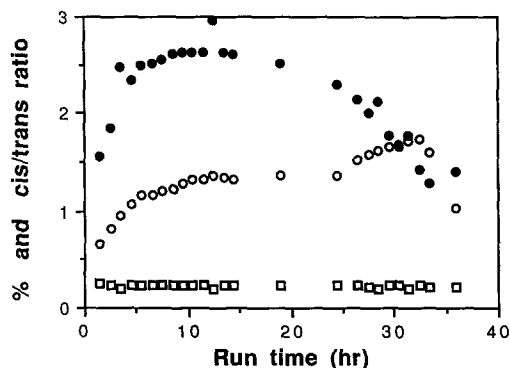


FIG. 12. The percentage of *n*-propylcyclopentane (○), 1-ethyl-2-methylcyclopentane (●), and the ratio of *cis-trans*-1-ethyl-2-methylcyclopentane (□) in the liquid products during the conversion of *n*-octane or a mixture of *n*-octane plus *n*-propylcyclopentane.

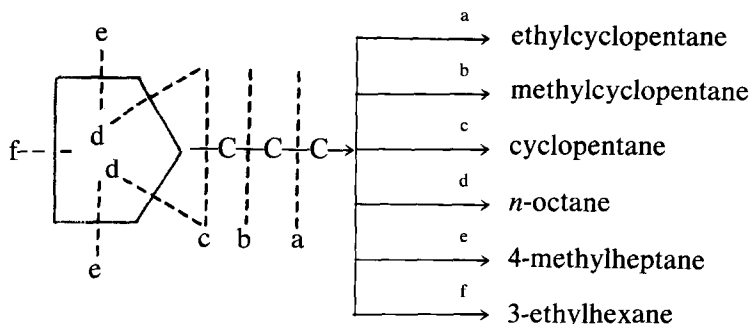
DISCUSSION

The aromatics produced in this study and those reported by Chevron workers (14, 15) from *n*-octane dehydrocyclization do not appear to be consistent with those required by the geometric constraints that require adsorption by the terminal carbon. For *n*-octane, terminal carbon adsorption followed by 1,6-ring formation would produce ethylbenzene as the only C₈ aromatic. The aromatics in both the present study and in Ref. (14, 15) are those expected for 1,6-direct-ring formation. However, both our and Chevron results show about equal amounts of ethylbenzene and *o*-xylene. Thus, the aromatics obtained from *n*-octane dehydrocyclization with the Pt-KL catalyst are similar to those obtained with Pt supported on nonacidic alumina.

The data for the conversion of *n*-propylcyclopentane can be compared to results obtained by Alvarez and Resasco (24) for methylcyclopentane. These authors state that Pt particles smaller than 30 Å were clearly seen for their Pt-KL sample and this observation, relative to Pt-SiO₂ catalysts, suggests that most of the metal is inside the zeolite. Statistically, hydrogenolysis of

methylcyclopentane should produce the following distribution of C₆ isomers: *n*-hexane (*n*), 40%; 2-methylpentane (2Me), 40%; and 3-methylhexane (3Me), 20%. For high dispersions of Pt on nonzeolite supports, the experimental values agree well with the values based upon the statistical value (25-27). Alvarez and Resasco (24) obtained 1 : 0.87 : 1 for the *n* : 2Me : 3Me ratio for their 1.05% Pt catalyst and 1 : 0.75 : 1 for their 0.13% Pt catalyst; this contrasts with the value of 1 : 1 : 0.5 expected for the statistical model. Because of the steric effect of the methyl group of methylcyclohexane, end-on adsorption would be expected to produce cyclopentane plus methane or 3-methylpentane from ring hydrogenolysis. The amount of 3-methylpentane is slightly larger than the statistical hydrogenolysis pathway but does not dominate to the extent expected for "molecular die catalysis." Unfortunately, these authors did not report the amount of cyclopentane produced during the conversion.

The situation is more complex with *n*-propylcyclopentane since there are six hydrogenolysis pathways leading to different products:



The experimental results are compiled in Table 4 together with the calculated data. The data appear to agree closely with a statistical model for ring hydrogenolysis since the experimental value for *n*-octane is 36% (40% for statistical); unfortunately, the in-

ability to separate 3-ethylhexane and the methyl heptanes prevents us from verifying this assertion to a greater extent. The hydrogenolysis of the *n*-propyl side chain does not agree with a selective terminal cracking mechanism; in fact, the data indicate just

TABLE 4

C₈-Alkane Distribution Calculated for Nonselective Hydrogenolysis of all C-C Bonds in *n*-Propylcyclopentane and the Normalized Experimental Distribution

	Experimental ^a	Calculated ^b
a. 3-Ethylhexane } b. 2-, 3-, and 4- Methylheptane	51.2 ^c }	37.5
c. <i>n</i> -Octane	28.3	25.0
d. Cyclopentane	10.7	12.5
e. Methylcyclopentane	6.12	12.5
f. Ethylcyclopentane	3.65	12.5

^a Average of four runs.

^b Calculated assuming statistical C-C bond hydrogenolysis.

^c These products could not be separated using the GC column needed for ¹⁴C counting.

the opposite. Hydrogenolysis increases in going from the terminal to the interior bonds of the *n*-propyl group to produce ethylcyclopentane:methylcyclopentane:cyclopentane = 1:1.7:2.9. By analogy, the products from *n*-octane hydrogenolysis show *n*-heptane:*n*-hexane:*n*-pentane = 1:1.14:1.28, any error because of the volatility of *n*-pentane and, to a lesser extent, *n*-hexane will cause an underestimation of these products.

We have plotted data for terminal cracking (C_7/C_6) versus aromatic selectivity in Fig. 13. On the basis of terminal cracking, our Pt-KL should be considered, according to Tauster and Steger, as out-of-channel. We have attempted to answer this question with TEM examination of the reduced and the used catalysts. The dominant structure for the platinum observed by TEM is that of particles in the 8- to 14-Å range with the very infrequent observation of a very large particle in the 200- to 500-Å size range. The particles in the reduced catalyst appear to be, on the average, about 2 Å smaller than in the used catalyst. We attempted to make measurements at high resolution but the zeolite crystal was unstable in the high-energy electron beam. The Pt crystallite size we obtained from TEM measurements certainly falls within the size range reported by others. In contrast to Besoukhanova *et al.*

(21), we did not observe long cylindrical particles and our catalyst contained particles in the 8- to 14-Å range rather than 10- to 25-Å diameter. From TEM measurements, Hughes *et al.* (14) indicated that the largest Pt particles were in the range 8–10 Å for reduction at 482°C; this is the particle size range we observe for Pt particles in our sample after reduction for 18 h. Hughes *et al.* (14) estimated particle sizes in the range of 10–30 Å from the chemisorption of CO following 1 h reduction. As the crystal grew with further reduction or use, the space between the metal and zeolite channel walls become smaller than the CO molecule, and some of the surface Pt atoms cannot chemisorb CO. Therefore, the decrease in CO chemisorption with increasing reduction temperature (or time) exaggerates the size of the PT crystal.

Alvarez and Resasco (24) report that the Pt particles in their catalyst were 30 Å and smaller and consider their particles to be in the interior of the zeolite. Miller *et al.* (28) recently reported results for a Pt-BaKL sample that contained 1.2 wt% Pt that, following reduction at 500°C, contained Pt particles consisting of five or six atoms. These authors contend that EDX data indicate that

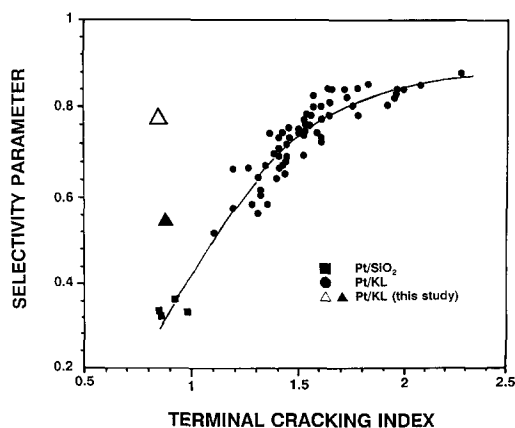


FIG. 13. Aromatization selectivity (aromatics/aromatics plus C₁-C₃) versus terminal cracking index (*n*-pentane/*n*-butane) for *n*-hexane conversion (from Ref. (22) and data at high (Δ) and lower (▲) conversion levels for *n*-octane from the present study.

TABLE 5

Comparison of Products Obtained from the Conversion of *n*-Octane with Pt-BaKL and Pt-KL Catalysts

	References (14, 15)	Present study
Catalyst	Pt-BaKL-866	Pt-KL
Pressure	6.9 bar	13.8 bar
Temperature	733 K	725 K
LHSV	6	ca. 1
Conversion (%)	30	27
C ₈ aromatics		
Ethylbenzene + <i>ortho</i> xylene	88	93.5
<i>Meta</i> - + <i>para</i> xylene	12	6.5
Methylheptanes/C ₈ aromatic	0.19–0.28 ^a	0.52
3-Ethylhexane/methylheptanes	0–0.51 ^a	0.15
2-Methylheptane	(8) ^b	18 ^c (21) ^{b,c}
3-Methylheptane	(34) ^b	26(28) ^b
4-Methylheptane	(58) ^b	41(51) ^b
3-Ethylhexane	—	15

^a Range of values because of overlap of 3-ethylhexane and 4-methylheptane.

^b Percentage based upon methylheptanes.

^c 2-Methylheptane peak corrected for coelution of toluene.

Pt is present in the imaged crystallites but that Pt particles could not be observed; thus, they infer that the Pt particles are very small and likely well dispersed in the zeolite crystals. Miller *et al.* (28) and Hughes *et al.* (14) appear to have prepared catalysts by similar procedures. Pt crystals of five to six Pt atoms should adsorb CO as easily as H since particles this small would not be excluded from adsorbing CO by contact with zeolite channel walls. At 500°C reduction Hughes *et al.* (14) report a dispersion of ca. 65% while Miller *et al.* (28) obtain greater than 100% from H adsorption for samples reduced at 500°C. It is not apparent why there should be such a dramatic difference between Pt dispersion for these two catalysts.

It should be apparent that the Pt dispersion in L zeolite is sufficiently small to make an absolute measure of their size and size distribution a demanding task. It should also be apparent that the Pt crystal size we obtain from TEM measurements are in the range reported by earlier investigators who claim that all, or a majority, of the Pt is present in the interior of the zeolite. Thus, on the basis of Pt crystal size measurements, our Pt-KL zeolite catalyst should be viewed as similar to those used in earlier studies.

While the question of the location of Pt in the catalyst remains uncertain, it is evident that Hughes *et al.* (14) have prepared at Pt-KBaL zeolite catalyst that retains a nearly constant activity during 8 months of operation with a refinery naphtha. The same catalyst designation, 0.8 Pt/BaKL-866, that was used for naphtha reforming was used for *n*-octane conversion at 460°C and 6.8 bar. The data obtained for the conversion of *n*-octane with this catalyst are compared in Table 5 with data we obtained for *n*-octane conversion with our Pt-KL zeolite catalyst. The aromatic isomers produced in both studies are very similar, and 88% or greater correspond to the isomers expected for direct six-carbon ring formation. The methylheptane distributions are similar in both cases and with a large excess of the least stable isomer, 4-methylheptane. As noted earlier, 4-methylheptane, 3-ethylhexane, and *n*-octane are the C₈ paraffins anticipated for ring opening by hydrogenolysis of *n*-propylcyclopentane. Hughes *et al.* (14) operated at 6.8 bar rather than the 13.6 bar used in the current study; thus, it is not unreasonable for us to obtain a lower aromatics to methylheptanes ratio at the higher pressure. Likewise, the higher hydrogen pressure used in our study would be expected to result in a lower conversion than the lower pressure used in Ref. (14). Overall, there is good agreement between the selectivity data generated during these two runs.

The catalyst prepared by Hughes *et al.* (14) had a long catalyst life, presumably because the Pt crystals were constrained to the channel cavities of the L zeolite. Since we obtained data for the dehydrocyclization of *n*-octane with our catalyst that is very similar to that reported by Hughes *et al.* (14), we conclude that either (1) our Pt is dispersed similar to that of Hughes *et al.* or (2) the location of small Pt crystallites does not materially affect the product selectivity for *n*-octane conversion.

The selectivity for aromatics formation during the conversion of *n*-alkane is indicated in Fig. 14. If anything, the aromatic

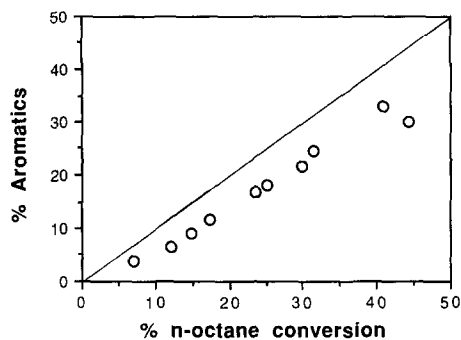


FIG. 14. The percentage of aromatics in the products versus conversion of *n*-octane to C_1 - C_7 alkanes and cycloalkanes plus aromatics.

selectivity is underestimated in Fig. 14 since any loss of mass for each sampling period has been considered to be cracking (C_1 - C_7) products. Losses also include compounds C_5 and higher in the gas phase that could not be analyzed for with the gas analyzer used in this study as well as any liquid loss that occurred during sample collection. Even so, the results in Fig. 14 indicate that the selectivity for aromatics is 56–75 wt% for the conversion of *n*-octane during the present study.

In Run 1 the propylene cyclopentane underwent only two conversions: hydrogenation

to *n*-propylcyclopentane and ring expansion to ethylbenzene. The conversion to ethylbenzene was about 4.5%. In Run 2 we note that ethylbenzene was not formed to a much greater extent even though 60 to 80% of the labeled *n*-propylcyclopentane underwent hydrogenolysis to isooctanes and C_8 products. This implies that it is easier to effect ring expansion when the alkene double bond is adsorbed presumably by π -Pt bonding than for an adsorbed propylcyclopentane; however, a more thorough study would be required to verify this. The absence of ring expansion of the added alkylcyclopentane is another strong reason to conclude that the catalyst does not possess acidic sites.

The data (Table 6) clearly show that an alkylcyclopentane intermediate does not produce aromatics very selectively with this Pt catalyst. This agrees with data generated in earlier studies. Csicsery and Burnett (10) found that ^{14}C -labeled 1,3-dimethylcyclopentane (2.5 vol%) in *n*-heptane produced toluene that contained only 8.8% of the ^{14}C in the total products; the activity in toluene and direct hydrogenolysis products (2,4-dimethyl pentane, 2-methylhexane, and 3-methylhexane) show that labeled toluene comprised only 13.6% of these products (Table 6). Hardy and Davis (13) found that

TABLE 6

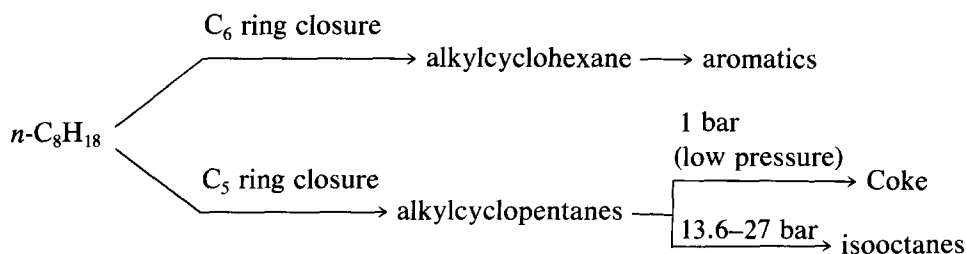
Percentage of Aromatics Produced in the Conversion of Alkylcyclopentanes

Reactant	Reaction conditions	[Aromatics/(aromatics + hydrogenolysis products)] $\times 100$	Reference
<i>n</i> -Heptane labeled (2.5 vol% 1,3 [^{14}C]dimethylcyclopentane)	482°C, 18 atm, 6:1 H_2 : hydrocarbon, 2% Pt-SiO ₂	13.6	10
<i>n</i> -Heptane (15% <i>n</i> -propylcyclopentane)	482°C, 13 atm, 9:1 H_2 : hydrocarbon, 0.6% Pt on nonacidic alumina	7.1	13
<i>n</i> -Heptane (8% 1-methyl-2-ethylcyclopentane)	482°C, 13 atm, 9:1 H_2 : hydrocarbon, 0.6% Pt on nonacidic alumina	8.3	13
<i>n</i> -Octane (2.4% <i>n</i> -[^{14}C]propylcyclopentane)	482°C, 13 atm, 7:1 H_2 : hydrocarbon, 0.6% Pt-KL	10–18	This study

the conversion of *n*-propylcyclopentane in *n*-heptane produced only 7.1% aromatics and 92.9% isooctanes. The present data agree rather well with the two studies discussed above. In contrast to this data, Lester (29) reported that a nonacidic Pt–Al₂O₃ catalyst was selective in producing aromatics from alkylcyclopentanes; however, he reported that acid sites in Pt reforming catalysts were more active for ring expansion than platinum. In view of the similarity of the data in Table 6 for the Pt–KL zeolite and nontraditional nonacidic Pt-supported

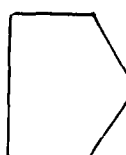
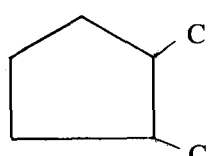
catalysts, it is of interest to compare the results obtained with the two types of catalysts in more detail.

It should not be surprising if the mechanism for hydrocarbon reactions conducted at 482°C, or higher, have minor side reactions in addition to the major reaction pathways. In the discussion below we first concentrate upon the major reaction pathways. For *n*-octane conversion over a Pt on a nonacidic support, Davis (12) proposed the following reaction pathways:



There is strong evidence that Pt on a nonacidic support catalyzes the conversion of *n*-alkanes to their branched isomers; it has been demonstrated frequently that the branched alkanes have a composition that is very close to the composition predicted for a nonselective hydrogenolysis of the cyclic three-, four-, or five-carbon ring compounds (e.g., (10, 13, 30–40)). Isomerization of *n*-alkanes, catalyzed by the metal func-

tion, is therefore proposed to occur by ring closure to a five-carbon ring compound followed by hydrogenolysis of a ring carbon–carbon bond. For a “nonacidic” Pt–Al₂O₃ catalyst, Hardy and Davis (13) found that the hydrogenolysis products from the two alkylcyclopentanes that could be formed by direct C₅ ring closure of *n*-octane agreed closely to those predicted for nonselective ring hydrogenolysis:

	Predicted	Observed
	<i>n</i> -Octane	33
	4-Methylheptane	42
	3-Ethylhexane	22 ^a
	Other	3
	<i>n</i> -Octane	46
	3-Ethylhexane	14 ^a
	2-Methyl-3-ethylpentane	10
	3,4-Dimethylhexane	8
	4-Methylheptane	21

^a Includes 3-methylheptane if formed.

The products common to both cyclopentane isomers prevent a determination of the relative contribution of each isomer during the conversion of *n*-octane over a nonacidic Pt–alumina; however, the isooctane products formed during *n*-octane conversion with a nonacidic Pt catalyst are predominately those predicted by hydrogenolysis of the above two alkylcyclopentane isomers (13, 14).

The hydrogenolysis of methylcyclopentane appears to show a high selectivity for the C–C bonds of the ring rather than producing significant quantities of methane and cyclopentane. This does not appear to be the case with *n*-propylcyclopentane. Hydrogenolysis to produce cyclopentane, methylcyclopentane, and ethylcyclopentane corresponds to ca. 20% of the total hydrogenolysis of *n*-propylcyclopentane. The GC column did not effectively separate *n*-hexane from cyclopentane and methylcyclopentane; however, the proportional counter output indicates that *n*-hexane contains little, if any, radioactivity. If hydrogenolysis of ring and side-chain C–C bonds (excluding the C–C bond that includes a terminal CH₃) were to occur at an equal rate, cyclopentane and methylcyclopentane should comprise about 29% of the products. The experimental value therefore indicates that an internal C–C bond of the side chain undergoes hydrogenolysis at about the same rate as a ring C–C bond.

For nonselective hydrogenolysis of the cyclopentane ring bonds, *n*-octane is expected to contain 40% of the radioactivity of the *n* + iso-C₈ alkanes. Unfortunately the large amount of *n*-octane in the liquid products spreads the ¹⁴C proportional counter retention time over a longer period than is the case for the isoalkanes and this introduces a large error in determining the relative amount of ¹⁴C in *n*-octane. Thus the percentage of the ¹⁴C in *n*-octane (relative to *n*- plus isooctanes) ranges from 18 to 36%; the average for the eight samples listed in Table 2 is 26%. This average value of 26% shows reasonable agreement with the value

of 33% obtained by Hardy and Davis (13) for the hydrogenolysis of unlabeled *n*-propylcyclopentane.

Alkylcyclohexanes are converted to aromatics with very few side reactions. Davis (41) added ¹⁴C-labeled methylcyclohexane to a naphtha and found that 87% of the ¹⁴C-labeled methylcyclohexane was converted to labeled toluene and 4.2% to benzene even under severe reforming conditions with an acidic Pt–alumina catalyst. With a nonacidic Pt–alumina 93% of the added methylcyclohexane was converted to toluene and 4% to benzene; only 2.6% of the ¹⁴C-labeled compound was converted to gas and alkane/naphthene liquid products.

One may express concern about the initial loss of activity in Figs. 1 and 3. However, it does not appear that this initial loss in activity is unique to our study. Hughes *et al.* (14) report a loss of at least 27% activity during 17 h of operation with a methylcyclopentane feed; an explanation for the decline in activity is not given. Tauster *et al.* (22) report the results of the conversion of a feed comprising *n*-hexane or 80% *n*-hexane/20% methylcyclohexane in an ECAT test; while this is considered to be an accelerated aging test, activity losses of 30–50% during 24 h of operation were not uncommon. In our studies we observe a relatively rapid initial decline followed by a period of slow decline in activity or a constant activity. Unfortunately, we did not determine whether the sulfur levels in the feed was in the low ppm or ppb levels. In any event, the activity loss, if due to poisoning, will not impact the conclusions of the present study unless poisoning impacts the two cyclization pathways, C₅ and C₆ carbon ring formation, to very different extents.

Most of the work with Pt–L zeolite catalysts has been concerned with the selective conversion of hexane to benzene; for this reaction the Pt–L zeolite catalyst is claimed to be vastly superior to conventional reforming catalysts. The advantage for Pt–L zeolite catalysts is not as great for higher alkanes such as *n*-octane. The present study

defines the role of alkylcyclopentanes as the intermediate responsible for conversion of *n*-octane to isooctane isomers with the monofunctional Pt–KL zeolite catalyst. The selectivity data for *n*-octane conversion resembles that reported earlier (14) for a catalyst that has a stable activity during 9 months of operation. It is presumed that the superior activity, selectivity, and aging properties are due to the location of the Pt in the channel and/or channel cavities, which limit Pt crystallite size to less than 12–14 Å and may impose special steric requirements for the chemisorption of the alkane reactant on the Pt. The current data was obtained with a catalyst that has a Pt crystal size range that is similar to those reported earlier. Furthermore, the conversion data for *n*-octane and *n*-propylcyclopentane using the Pt–KL zeolite catalyst are very similar to data obtained with catalysts based on other nonacidic supports where the Pt crystals cannot be located in a zeolite-type channel. Thus, for *n*-octane conversion, it appears that the Pt in L zeolite catalysts has selectivities that are similar to Pt on other nonacidic supports.

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