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Conversion of Labeled Hydrocarbons

VI. n-[1-^{14}C-] and n-[4-^{14}C-] Heptane over Pt–Sn– and Pt–Re–Al_2O_3 Catalysts[1]

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The ^{14}C distribution in toluene from the aromatization of n-[1-^{14}C-] and n-[4-^{14}C-] heptane over both Pt–Sn– and Pt–Re–Al_2O_3 catalysts was that expected for a direct 1,6-ring closure. The results using the bimetallic catalysts were in excellent agreement with results previously reported for a metal oxide catalyst (chromia) and a metal catalyst (Pt) suggesting that dehydrocyclization follows a similar mechanism over all three catalyst systems.

INTRODUCTION

The dehydrocyclization of alkanes is an important and widely studied reaction which is catalyzed by both metal and metal oxide catalysts. A primary concern is whether the same mechanism is followed over both types of catalyst. Anderson (*1*) recently concluded that "Although reactions over nonacidic metal oxide catalysts possess some superficial similarities to reactions over platinum catalysts, on the whole, the two systems are sufficiently distinct that, at a mechanistic level, they are worth treating independently." In any mechanistic consideration for alkane dehydrocyclization, the first level is a description of the cyclization. A prime consideration is the number of carbons that make up the ring that is initially formed. A considerable body of evidence has been reported for alkane conversion over metal films and high metal content catalysts which supports a direct 1,5-ring closure (*1*, *2*) at lower temperatures. On the one hand, workers offer evidence to support a direct 1,5-ring closure at higher temperature on low loading Pt catalysts (*3*) and even at the higher pressures encountered in reforming (*4*). On the other hand, strong support for a direct 1,6-ring formation at reforming temperatures (*5–8*) and even at reforming pressures (*9*) has been reported. In this communication we present data for ^{14}C labeled heptane dehydrocyclization over metal alloy catalysts that have bearing on the two concerns that were detailed above.

EXPERIMENTAL METHODS

Catalysts

Pt–Sn–Al_2O_3–K. Nonacidic alumina (*10*) (ca. 1.0 wt% K; 200 m^2/g) was impregnated with an acetone solution of chloroplatinic acid and stannous chloride (Pt:Sn = 1:4 mole ratio) to give a final catalyst which was analyzed to contain 0.6 wt% Pt and 1.5% Cl.

Pt–Re–Al_2O_3–K. Nonacidic alumina (ca. 1.0 wt% K; 200 m^2/g) was impregnated with an aqueous solution of chloroplatinic acid and potassium perrhenate using suffi-

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[1] Previous papers of the series: V, *J. Catal.* 29, 395 (1973); IV, reference *7c*; III, reference *15*; II, reference *7b*; I, reference *7a*.

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cient water to just fill the pore volume of the alumina. The catalyst was dried at 120°C before the reduction at 525°C.

E-601. This was a commercial Pt–Re–Al_2O_3 catalyst supplied by Engelhard Industries.

Procedure

The reactions were carried out in a flow reactor using a syringe pump to provide the reactant flow, a Pyrex reactor, liquid product collector, and burette to measure gas flow. Approximately 25 ml of silicone carbide chips on top of the catalyst served as a preheater.

The Pt–Sn– and Pt–Re–Al_2O_3–K catalysts were pretreated at 525°C in a 5 ml/min flow of hydrogen. The pretreatment for the E-601 catalyst followed the prescription of the supplier including the presulfiding but omitting the chlorination.

TABLE 1

Conversion of *n*-[1-^{14}C-] and *n*-[4-^{14}C-]Heptane over Pt–Sn–Al_2O_3–K and Pt–Re–Al_2O_3

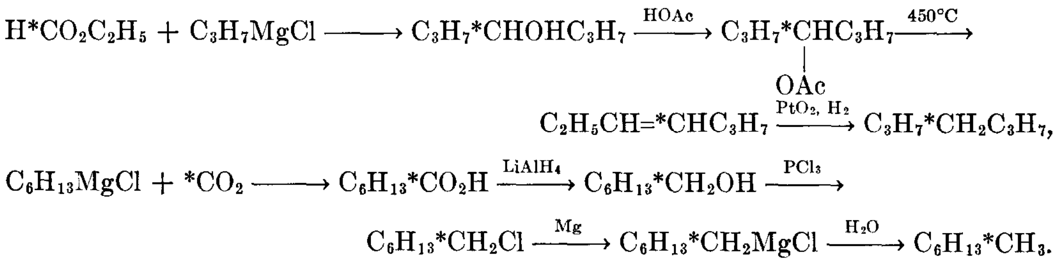
Catalyst	Time (min)	Sample	Methyl ^{14}C in toluene (%)	
			charge = 1-^{14}C-	4-^{14}C-
Pt–Sn–[a]	35	1	52	0.57
	75	2	49	0.29
Pt–Re–[b]	40	1	34	4.08
	70	2	32	2.45
	120	3	32	

[a] LHSV, 0.5; Temp, 482°C, H_2:hydrocarbon, 1:1.5; H_2 flow, 5 ml/min.

[b] Same as above except the heptane charge contained approximately 3 wt% *sec*-butylamine.

During the runs with the commercial E-601 catalyst approximately 3 wt% *sec*-butylamine was added to the alkane charge to try to eliminate the acid catalyzed reaction(s).

The ^{14}C hydrocarbons were synthesized by the following reaction schemes (*C represents ^{14}C):



$$H{*}CO_2C_2H_5 + C_3H_7MgCl \longrightarrow C_3H_7{*}CHOHC_3H_7 \xrightarrow{HOAc} \underset{\displaystyle OAc}{C_3H_7{*}CHC_3H_7} \xrightarrow{450^\circ C}$$

$$C_2H_5CH{=}{*}CHC_3H_7 \xrightarrow{PtO_2,\ H_2} C_3H_7{*}CH_2C_3H_7,$$

$$C_6H_{13}MgCl + {*}CO_2 \longrightarrow C_6H_{13}{*}CO_2H \xrightarrow{LiAlH_4} C_6H_{13}{*}CH_2OH \xrightarrow{PCl_5}$$

$$C_6H_{13}{*}CH_2Cl \xrightarrow{Mg} C_6H_{13}{*}CH_2MgCl \xrightarrow{H_2O} C_6H_{13}{*}CH_3.$$

The liquid products were collected at intervals of time. For the runs using pure labeled heptane, the toluene product was separated by liquid chromatography using dry silica gel with isopropyl alcohol as the eluting agent. For the run with the ^{14}C labeled heptane-*n*-octane mixture, the toluene product was trapped by passing the appropriate effluent peak from a Carbowax 20M glc column (operated at 90°C isothermally) through about 4 ml of toluene at 0°C. The procedure to degrade the toluene to determine the methyl label has been described previously (7a). Briefly, the toluene was oxidized to benzoic acid which in turn was decarboxylated with hydrazoic acid (the Schmidt reaction) to obtain the methyl carbon as carbon dioxide or was burned to carbon dioxide using the van Slyke procedure to obtain the total carbon as CO_2. The CO_2 was trapped in a sodium hydroxide solution, then precipitated as $BaCO_3$, and the radioactivity was determined using a liquid scintillation counting procedure.

The liquid product was analyzed for conversion to aromatics using glc with a Carbowax 20M column. Analysis of the

TABLE 2

Conversion of n-Octane over Pt–Re–Al_2O_3 Catalyst with *sec*-Butylamine Present[a]

Run	Time (min)	Conversion (%)	Aromatic distribution (mole%)			
			EtBz	OX	MX	PX
Pt-Re-4[b]	45	35	35.3	60.0	4.23	0.65
	130	35	37.3	59.8	2.10	0.84
	270	24	37.4	60.0	1.77	1.06
	320	22	40.2	57.2	1.48	1.23
Pt-Re-7[c]			35.1	56.0	6.1	2.8
			42.8	49.1	5.5	2.6
Pt-Re-8[d]			42.1	43.6	10.0	4.4
			43.4	44.8	8.9	2.9

[a] Conditions same as in footnote *b* to Table 1.

[b] Numbers refer to repeat runs using a fresh catalyst for each run.

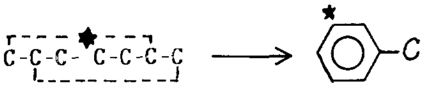
[c] Distributions for the fourth and fifth sample taken after ca. 300–400 min.

[d] Distributions for the third and fourth sample taken after ca. 300–400 min.

aromatics from the runs with n-octane was done by glc using a Bentone-3,4-diisodecyl phthalate column.

RESULTS

For the ^{14}C labeled heptanes used in this study we have the following 1,6-ring closure possibilities:



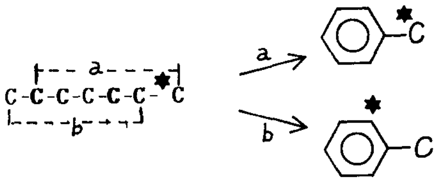


Table 1 presents the amount of methyl labeled toluene obtained for the conversion of the two labeled heptanes over the Pt–Sn and the Pt–Re catalysts. It is noted that with the Pt–Sn catalyst the experimental methyl label and that predicted based on the 1,6 direct ring closure schemes shown above are in excellent agreement. However, with the commercial E-601 catalyst the agreement between the experimental and predicted results are poor for both reactants.

For the dehydrocyclization of n-octane, the direct 1,6-ring closure allows ethylbenzene and *ortho*-xylene formation but not *meta*- and *para*-xylene. An attempt was made to carry out the n-octane dehydrocyclization over a Pt–Re catalyst supported on "nonacidic" alumina. The alumina is "nonacidic" due to the potassium ions incorporated in the material during precipitation from a potassium aluminate solution by precipitation by adjusting the pH with carbon dioxide. However, this catalyst was completely inactive for n-octane dehydrocyclization. The reason that the alkali metal is such a severe poison for the Pt–Re catalyst is not known; however, we suspect that the potassium ion stabilized the rhenium in an oxidation state that was resistant to hydrogen reduction.

Since the nonacidic Pt–Re catalyst could not be used for the alkane dehydrocyclization, we turned to a commercial, acidic catalyst. An equilibrium aromatic distribution was obtained for n-octane conversion with this catalyst with *meta*-xylene as the major product. In order to determine the primary C_8 aromatic distribution from the acidic, commercial Pt–Re catalyst, we tried to eliminate the dual-functional acid catalyzed isomerization by adding about 3 wt% *sec*-butylamine to the hydrocarbon charge. Results for the conversion n-octane are presented in Table 2. The C_8-aromatics are what would be expected for a direct 1,6-ring closure for the first run (Pt–Re-4); at later time on stream the aromatics allowed by 1,6-ring closure make up greater than 97% of the C_8-aromatics.

Encouraged that we could easily suppress the acidic function using *sec*-butylamine, we then ran the two ^{14}C labeled n-heptanes with the results shown in Table 1. It was

TABLE 3

Aromatic Products from the Dehydrocyclization of *n*-[1-^{14}C-] Heptane-*n*-octane Mixture (with 3 wt% *sec*-Butylamine) over Pt–Re–Al_2O_3 (E-601)[a]

Time (min)	Conversion to aromatics (%)[b]	Methyl ^{14}C in toluene (%)	C_8 isomer (% of C_8 aromatics)[c]			
			EB	OX	MX	PX
40	75	40.7	26.4	41.7	18.0	8.9
85	50	40.2	35.5	43.1	14.6	6.8
125	35	32.2	38.4	42.1	13.3	6.2

[a] Conditions same as in footnote *b* to Table 1.

[b] Conversion is total for both alkanes and is approximate due to the large number of products formed.

[c] EB = ethylbenzene, OX = *ortho*-xylene, MX = *meta*-xylene, PX = *para*-xylene.

obvious that we had not poisoned as many of the acid sites in these runs with *n*-heptane as we had in run Pt–Re-4 with *n*-octane or that *n*-heptane underwent extensive conversion to toluene by a pathway other than a direct 1,6-ring closure.

We then repeated the runs with *n*-octane, each time subjecting a fresh catalyst to the "same" reduction and run procedures. The results for Pt–Re-7 and -8 runs indicated that the poisoning with *sec*-butylamine was not equally efficient in repeat runs.

In order to be able to compare the two reactants under identical conditions, we ran a mixture of *n*[1-^{14}C-] heptane and *n*-octane (approximately a 1:1 mole ratio). Results for this run are presented in Table 3. About 25% of the C_8-aromatics were *meta*- and *para*-xylene, isomers that are not allowed by a direct 1,6-ring closure. Also note that more of the *ortho*-xylene isomer is formed than ethylbenzene. Thus, the C_8-aromatics are similar to the other Pt–Re runs except that this run was the least selective for the direct 1,6-closure products, ethylbenzene and *ortho*-xylene. The amount of the methyl labeled toluene was approximately 40%. This value of 40% methyl label would be consistent with 20% of the total ^{14}C isotope being at a location other than that expected by direct 1,6-ring closure. Thus, for the competitive conversion of the two alkanes, the amount of 1,6-ring closure is the same for each alkane.

DISCUSSION

Dehydrocyclization studies of *n*-heptane labeled at the C-1 and C-4 positions over chromia (*7*a, b) and over Pt–Al_2O_3–K (*7*c) catalysts were consistent with 80% or more of the toluene being formed by a direct 1,6-ring closure mechanism (C_6). Furthermore, partial degradation of the aromatic ring of the toluene obtained over Pt on nonacidic alumina indicated that if a cyclopentane was an intermediate in a major reaction pathway, severe restrictions on the subsequent ring expansion would make the cyclopentane pathway (C_5) equivalent to a C_6 pathway. Professor Pines later reported preliminary results for *n*-[1-^{14}C-] heptane dehydrocyclization over nonacidic Pt/Al_2O_3 which confirmed our finding of 80% of the ^{14}C at positions expected for C_6 cyclization (*11*). However, on the basis of these results (*11*) and others, Professor Pines believed that, while direct C_6 was the major pathway, other pathways, including 1,7- and 1,5-ring closure followed by ring isomerization, were involved.

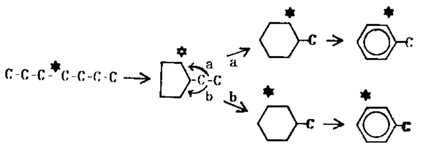
Our (*7*a, b) experimental results for ^{14}C labeled heptane aromatization over unsupported chromia and chromia supported on acidic alumina are in excellent agreement with those reported by Pines and Gotschel

(*12*). The only experimental difference was observed with chromia on nonacidic alumina where our results (*7*a, b) show about 80% of the ^{14}C label at positions expected for the C_6 pathway while those obtained by Pines would indicate a nearly uniform ^{14}C label at each carbon position in the toluene product at an early time-on-stream (*13*). Pines advanced a cycloheptane intermediate to explain the nearly equal label distribution. Mitchell (*14*) also obtained a low label at the positions expected for C_6 closure with his chromia on nonacidic alumina. Davis and Fejes (*15*) obtained about 80% or more of the ^{14}C label at the positions expected for a C_6 closure with 1-[1-^{14}C-] heptane using a chromia on nonacidic alumina catalyst.

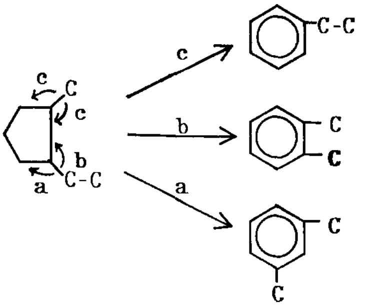
The present results with *n*-[1-^{14}C-] and *n*-[4-^{14}C-] heptane over both Pt–Sn– and Pt–Re– bimetallic catalysts are in good agreement with our earlier results with Pt and with chromia catalysts where 80% or more of the toluene was labeled as expected for a C_6 closure. Thus, we obtain the same tracer results over three general catalyst systems: a metal oxide (supported and unsupported chromia), a metal (Pt on nonacidic alumina), and bimetallic catalysts (Pt–Sn on nonacidic alumina and Pt–Re on acidic alumina with butylamine present).

Fogelberg *et al.* (*6*) reported results for the dehydrocyclization of several alkanes over Pt on a low surface area, nonacidic alumina and concluded that cyclization occurred by C_6 closure followed by dehydrogenation to aromatics. The aromatics not allowed by a C_6 closure resulted from an isomerization of the charge prior to cyclization. Davis and Venuto (*8*d) reported results for the dehydrocyclization of a number of alkanes over Pt on a high area, nonacidic alumina that supported and extended the results of Fogelberg *et al.* Thus, there are results with unlabeled alkanes that also support a direct C_6 closure.

However, not all investigators obtain results which support a direct six carbon ring cyclization. Using a Pt–SiO_2 catalyst, Callender *et al.* (*4*) found that at short residence times with *n*-heptane at a total pressure of 225 psi at least 90% of the cyclics were formed by a C_5 closure. To these workers, it seemed probable that the toluene in the product came from the dehydroisomerization of ethylcyclopentane but not the 1,2-dimethylcyclopentane. They implied that C_6 closure did not occur. For toluene formed from an ethylcyclopentane intermediate during *n*[4-^{14}C-] heptane dehydrocyclization we would have the following:



Neglecting a small possible isotope effect, we would be required to obtain an equal label at ring position C-2 and C-3 since pathways a and b are equivalent. Instead, we previously found about 20 times as much label at C-3 as at C-2 (*7*c). Thus, our results are not compatible with ethylcyclopentane being the pathway for toluene formation from *n*-heptane. Likewise, we have reported that aromatics from *n*-octane over a Pt on nonacidic alumina were essentially ethylbenzene and *ortho*-xylene (*8*). Callender *et al.* found only ethylcyclopentane and 1,2-dimethylcyclopentane in the conversion of *n*-heptane. If the same C_5 selectivity applies for *n*-octane, only *n*-propyl- and 1-ethyl-2-methylcyclopentane would be formed. According to Callender *et al.* (*4*) the *n*-propyl isomer would only lead to ethylbenzene. Also, 1-ethyl-2-methylcyclopentane should lead to nearly equal amounts of *ortho*- and *meta*-xylene by pathways a and b and ethylbenzene by pathways c in the reaction scheme outlined below. But the amount of *meta*-xylene was insignificant when compared to the amount of *ortho*-xylene when we converted *n*-octane over Pt at 200 and 400 psi. Hence, we must conclude (a) the cyclopentane intermediates do not make a significant contribution to the aromatics formation over the metal function or (b) an extremely unique ring expansion is operating which allows pathway b but excludes pathway a in the above scheme. Thus, aromatic distributions from *n*-octane dehydrocyclization (at 1 and at 14–27 atm total pressure) as well as the ^{14}C results with *n*-heptane, argue against a cyclopentane intermediate in the aromatic formation over the metal function.



Dautzenberg and Platteeuw (*16*) studied the conversion of *n*-hexane and 2-methylpentane at about 9 atm. They concluded that the five and six member rings are formed in parallel reactions. However, they arrived at the rather surprising conclusion that the five member ring does not undergo direct expansion to a six member ring but, rather, the five member ring undergoes isomerization to a structure with at least six carbons in a straight chain. This would require that hydrogenolysis of the cyclopentane ring, once formed, be more rapid than the platinum catalyzed ring expansion reaction.

C_5, rather than C_6, cyclization appears to be the dominant reaction pathway at low temperatures (225–325°C) (*1, 2*). However, these low temperature results are obtained on metal films or high (15–30%) metal content Pt catalysts; both of these conditions favor large metallic particles rather than the much smaller particles to be found in our catalysts. Also to be considered is the fact that we find alkanes do not inhibit the dehydrogenation of a cycloalkane at 400°C to the drastic extent that they do at 482°C where in a competitive conversion the alkane and cycloalkane each undergo conversion in nearly the same ratio that they are present in the charge. Consequently, there is considerable doubt, on the basis of metal crystal size and temperature, in extrapolating the low temperature studies to the conditions used in this study.

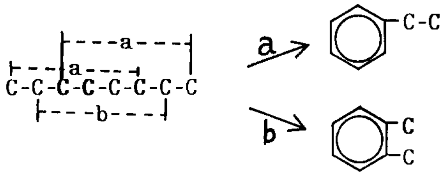
The use of the two names, cyclodehydrogenation and dehydrocyclization, by early workers in the field emphasized their uncertainty as to whether the cyclization step occurred early or late in the several possible dehydrogenation steps of the reaction pathway. Proposed cyclization steps have varied from a di-adsorbed alkene (*5*b) to a noncatalyzed, gas phase cyclization of a linear triene (*21, 22*). ^{14}C labeled potential intermediates for hexane aromatization have been added to unlabeled alkane, various alkenes, dienes and trienes as well as cycloalkane reactants. The ^{14}C distribution in the reactant, intermediates and aromatic products was interpreted to support a gas phase cyclization of a triene. While this is the most appealing chemical reaction that leads directly to a six carbon ring, we should keep in mind the fact that the reaction scheme involving a gas phase cyclization is the scheme that is most succeptible to a "kinetic disguise" (*23*) and a most difficult scheme to experimentally prove using added labeled compounds.

Bimetallic catalysts are now important for the reforming process where Pt–Re seems to be the choice combination for commercial operations. A number of patents have been issued on the Pt–Sn system but little fundamental reaction mechanism work has been reported. Karpiński and Clarke (*17*) studied the reaction of n-hexane over Pt–Sn films in the temperature range 285–360°C but used a Pt:Sn ratio that was higher in Pt than the mixture that we used in the present study. They found both C_5 and C_6 closure over Pt and the alloys. However, the proportion of C_6 closure increased with temperature to become dominant at the highest temperature (360°C). Also, at their highest temperature they found a decreasing contribution of C_5 cyclization with increasing Sn content until at a 30 atom % tin the cyclization was by C_6 closure. This suggests that these workers would have obtained only C_6 closure over their alloy catalysts under our reaction conditions.

Van Schaik *et al.* (*18*), in a summarization of their experimental work on Pt and Pt–Au alloy catalysts along with selected literature reports, state that for pure platinum the prevailing reaction is isomerization and that cyclization occurs by ring closure through an α, α, Ω adsorption (C_5 closure). [Such α, α, Ω intermediates are also used by Corolleur and co-workers (*19*) in their discussions of isomerization of alkanes.] Alloys with approximately 10% Pt catalyze predominately cyclization. With very dilute Pt alloys, the prevailing reactions are isomerization (probably by a "nonclassical" carbonium ion mechanism) and ring enlargement. In any event, the above workers are in agreement with us in the general conclusion that alloys have different cyclization selectivities than the pure metal.

Plunkett and Clarke (*20*) reported results for Ir and Ir–Au films for the conversion of n-hexane. They inferred that the C_6-ring structure forms directly and not through a C_5-ring intermediate. They also found a superior selectivity for benzene production over the alloys compared to pure Ir; this was due to the decrease in the hydrogenolysis rate for the alloys. Their experimental results and conclusions for Ir and Ir–Au alloys are in excellent agreement with our Pt–Sn studies.

The dehydrocyclization of n-octane to form six carbon rings can proceed by two pathways:



Based on the change in the selectivity for ethylbenzene and *ortho*-xylene caused by (a) adding metal promoters to Pt, (b) adding gaseous promoters or (c) changing the Pt loading, we concluded (*8*) that decreasing the electron concentration of Pt would favor the formation of *ortho*-xylene by pathway b at the expense of ethylbenzene. Pathway b involves two secondary C–H bonds while pathway a involves one secondary and one primary C–H bond; consequently, pathway b, on the basis of C–H bond breaking, should be energetically more favored. An extension of this reasoning would show two cyclization pathways leading to cyclopentanes by breaking only secondary C–H bonds so that we would expect at least some cyclopentane product. However, we do not obtain a significant amount of cyclopentanes even with the Pt–Sn or Pt–Re catalyst. Thus, our explanation of aromatic selectivity changes would lead us to a prediction of an increasing contribution of C_5 cyclization with the alloy catalysts but the experimental results do not support this prediction. It is possible that the cyclopentanes that were formed in our study (*9*) underwent hydrogenolysis to form isooctanes while the catalyst used by Callender *et al.* (*4*) was much less active for hydrogenolysis of cyclopentanes. Since 5 to 10 times more isooctanes than C_8-aromatics were formed in our study (*9*), this appears to be a reasonable explanation for the great differences in the experimental results. We would also expect the C_5 reaction pathway to become more important at higher hydrogen pressure for the low loading, high metal surface area catalysts. This is due to the fact that a high proportion of the metal atoms will be surface atoms for metal crystallite sizes in the range of 10–40 A and, as the hydrogen pressure becomes larger, the chemisorbed hydrogen atoms will serve the same function as adding a second metal to the Pt. The high proportion of surface atoms would lead to this conclusion even without requiring a hydrogen solubility in the platinum metal. Thus, we expected to find a large increase in cyclopentane isomers in the liquid product from *n*-octane conversion over Pt at 400 psi; however, we did not. Again, the presence of isomerized octanes may be due to our Pt catalyst having a high hydrogenolysis activity for cyclopentanes.

In summary, the present and previously reported ^{14}C tracer studies are consistent with a direct C_6 ring formation. The various catalysts—chromia, (both unsupported and supported on acidic and nonacidic alumina), Pt on nonacidic alumina, and the bimetallic Pt–Sn– and Pt–Re– supported on alumina—gave the same ^{14}C distribution in the aromatic products and this is consistent with a common cyclization scheme for all three catalyst types.

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