

Selective Ring Opening of Naphthenic Molecules

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Ring opening as practiced in hydrocracking of naphthenic molecules results from multiple cleavages of both endo- and exocyclic C–C bonds. Selective ring opening requires that only one endocyclic C–C bond per naphthene ring be severed, preserving thereby reactant molecular weight. The products of selective ring opening are alkanes and alkylnaphthenes. Over hydrocracking catalysts the yield of alkanes with the same number of carbon atoms as the reactant naphthenes is unacceptably low as a result of extensive dealkylation of alkylnaphthenes and secondary cracking of alkanes. Alkylcyclopentanes, in contrast, selectively ring open by hydrogenolysis over a number of noble metal catalysts. Under similar reaction conditions the selective ring-opening rates of alkylcyclohexanes are, however, one to two orders slower than those of alkylcyclopentanes. Addition of a ring-contraction acidity function converts alkylcyclohexanes into more easily ring-opened alkylcyclopentanes, greatly facilitating selective ring opening. Selective ring-opening rates and selectivities are optimum when ring isomerization occurs by a nonbranching ring contraction. Branching ring contraction, creating increased numbers of ring substituents, is detrimental to both ring-opening rates and selectivities. When an effective acidity function is coupled with a high-activity hydrogenolysis metal, such as iridium, the resulting bifunctional catalyst system greatly outperforms conventional hydrocracking catalysts for the selective conversion of naphthenes to alkanes. © 2002 Elsevier Science (USA)

Key Words: ring opening; hydrogenolysis; acidity; iridium catalysts; isomerization; ring contraction; bifunctional catalysts.

1. INTRODUCTION

Future middistillate diesel fuels will be required to meet higher quality standards as a means to lowering tailpipe emissions. Key product quality requirements for diesel-range distillates include ultra-low-sulfur contents and reduced multiring aromatic concentrations. Lower product densities and higher cetane numbers are also anticipated (1, 2). Commercially proven upgrading technologies include aromatics saturation (ASAT) and hydrocracking (3–6). ASAT improves the cetane number and reduces the

density of middistillate fuels while maintaining the gasoline/diesel product balance by minimizing cracking to light paraffins. The ultimate cetane number and density from ASAT alone are, however, limited by feedstock composition. Hydrocracking, in contrast, improves middistillate quality by concentrating minimally branched, high-cetane-value alkanes in the middistillate boiling range by cracking naphthenes and branched alkanes to lighter, gasoline-range products.

A potential route to a low aromatics, reduced density, high-cetane-value diesel fuel is ASAT of a low-sulfur mid-distillate stream followed by selective ring opening (SRO) of naphthenic rings to alkanes. SRO is defined as opening naphthene rings without loss of reactant molecular weight. Although ASAT as a route for upgrading middistillates has been described in detail (7), the potential use of SRO has only recently been described (8, 9). A simplified scheme for the proposed ASAT plus SRO naphthene upgrading chemistries is shown in Fig. 1. Saturation of naphthalene to decalin, requiring the addition of 5 mol of hydrogen, improves both density and cetane number. However, the lowest density achievable by complete saturation of naphthalene is near 0.90 and the maximum cetane number is about 38. To comply with anticipated diesel specifications of densities <0.85 and cetane numbers >40 product improvements are needed. Ring opening decalin to C₄-cyclohexanes or decanes is shown to significantly enhance both product cetane number and density. Thus SRO offers a new approach for meeting future diesel quality standards. To aid the discussion of the rather complex chemistries associated with SRO it is informative to consider Fig. 2, which outlines transformations likely to occur during the conversion of multiring aromatics to alkanes. Complete saturation of multiring aromatics to multiring naphthenes prior to SRO is desired. Metal and acid site promoted hydrocracking and dealkylation reactions must be avoided to minimize losses in middistillate yield. SRO of both five- and six-membered naphthene rings is an essential reaction. Controlling the interconversion of six- and five-membered rings via an acid-catalyzed ring-contraction step is also of special importance, since, as will be shown, selective conversion of

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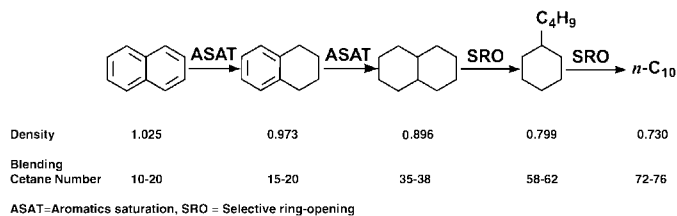


FIG. 1. Aromatic saturation of multiring aromatics followed by selective ring opening provide density and cetane number benefits.

six-membered naphthene rings to five-membered naphthene rings greatly influences ring-opening rates and selectivities. Secondary isomerization of product alkanes must be avoided, as increased branchiness greatly reduces cetane values. The research reported here emphasizes the use of model one- and two-ring naphthenic molecules. Saturated molecules were targeted because SRO is a metal-driven chemistry and multiring aromatics and naphtheneoaromatics are readily hydrogenated to naphthenes under typical ring-opening reaction conditions (10). The focus of this paper centers on the final ring-opening step, the selective conversion of one-ring naphthenes to alkanes.

2. EXPERIMENTAL

Metal-loaded catalysts were prepared by conventional incipient witness impregnation of standardized metal solutions onto well-characterized noncrystalline and zeolitic and microporous supports. Catalyst preparation particulars

can be obtained by consulting Refs. (8, 11). Metal analyses were in all cases in agreement with nominal values.

Model compounds investigated included methylcyclopentane (MCP), methylcyclohexane (MCH), *n*-pentylcyclopentane (PCP), *n*-butylcyclohexane (BCH), decalin, perhydroindan, bicyclo[3,3,0]octane, ethylcyclopentane (ECP), 1,1-, 1,2-, and 1,3-dimethylcyclopentanes (1,1-DMCP, 1,2-DMCP, and 1,3-DMCP), and 1,2,4-trimethylcyclohexane (1,2,4-TMCH). All the above compounds are commercially available except PCP. 1-Pentylcyclopentene was prepared by Professor H.E. Ensley of Tulane University. The olefin intermediate was hydrogenated to PCP by us over a 10% Pd/carbon catalyst at 5520 kPa at 327–373 K.

Methylcyclopentane and methylcyclohexane ring-opening studies were carried out in a 25-cm³ stainless-steel, fixed-bed, downflow reactor capable of operating at pressures up to 5500 kPa and temperatures up to 823 K. The reactor was heated by a fluidized sand bath which provided near-isothermal operation throughout the entire reactor zone. Pure reactants were fed to the reactor by a Ruska feed pump. The upper portion of the reactor contained inert mullite beads, which served as a preheat zone and also minimized dead space volume. Total reactor effluent was analyzed online by a Wasson-engineered GC system equipped with a 60-m capillary column having a methylsilicone stationary phase. All products ranging in molecular weight from methane through the isomeric xylenes were verified by GC/MS analyses.

n-Pentylcyclopentane, *n*-butylcyclohexane, decalin, perhydroindan, and bicyclo[3,3,0]octane ring-opening

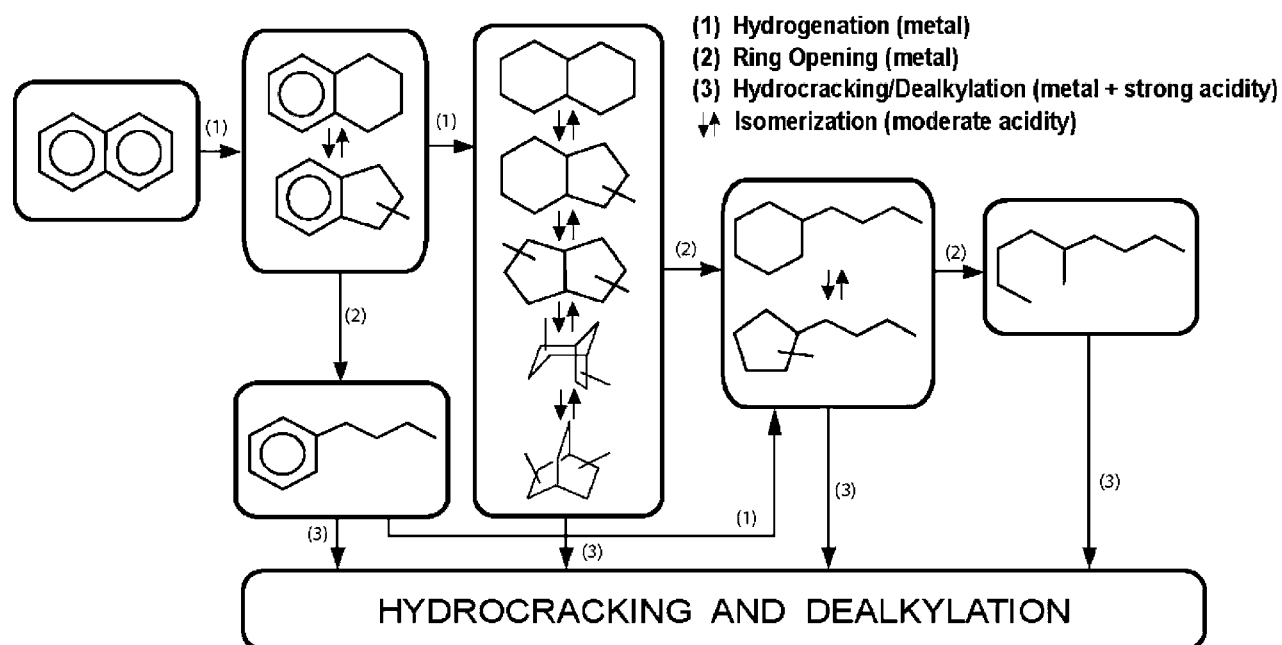


FIG. 2. Key reactions during the conversion of multiring aromatics to paraffins.

reactions were carried out in a once-through, downflow, fixed-bed, stainless-steel reactor heated by an infrared furnace. The unit is designed to operate at pressures up to 8300 kPa and temperatures up to 773 K. The reactants, 20% in *n*-heptane or neat, were fed to the reactor by an ISCO syringe pump. Liquid product samples were collected and analyzed by GC/MS for ring-opening and isomerization products. Total effluent was routinely analyzed by online GC to monitor conversion and cracking yields.

Ethylcyclopentane, 1,1 dimethylcyclopentane, 1,2-dimethylcyclopentane, 1,3-dimethylcyclopentane, and 1,2,4-trimethylcyclohexane experiments were carried out in a once-through, fixed-bed, downflow stainless-steel reactor heated by an infrared furnace. The unit is designed to operate at pressures up to 7000 kPa and temperatures between 300 and 733 K. A coil of 1/8-in. stainless-steel tubing heated to 473 K served as a liquid feed and gas mixer/preheater. Reactor temperature was measured and controlled by a thermocouple placed in the catalyst bed. Liquid product samples were collected for combined GC/MS–GC/FID analyses. Total effluent was analyzed by online GC. All downstream process lines and the Mitey-Mite pressure controller were heated to 473–523 K. C₁–C₁₀ hydrocarbon products were analyzed on a HP5890 GC equipped with FID and a 30 m × 0.32 mm ID DB-1 column with a film thickness of 1.0 μm.

3. RESULTS AND DISCUSSIONS

3.1. Naphthene Ring-Opening Pathways

Ring opening of naphthenes can occur by three different reaction chemistries. These are compared in Table 1. Free radical conversion is one possible reaction pathway and is initiated by either pyrolysis at high temperature or by addition of radical initiators formed via thermal decomposition of reactive compounds (12, 13). Naphthenoaromatics, such as tetralin, are quite reactive and radical like ring opening to butylbenzene has been reported (14); secondary cracking

and dealkylation of butylbenzene, as well as dehydrogenation of tetralin to naphthelene, are substantial competing reactions which severely limit ring-opening yields. Since radical cracking of product alkanes is 5- to 50-fold faster than those of naphthenes of equivalent carbon number (12) it is difficult to maintain high ring-opening yields, especially at high conversion levels.

Acid-catalyzed carbocation cleavage of ring C–C bonds is a second possible ring-opening route. Naphthenic molecules are activated by either direct formation of a cationic species by hydride abstraction by a Lewis acid or by protonation of an olefin intermediate formed by naphthene dehydrogenation over a metal function. Ring opening and/or cracking may proceed by a β-scission mechanism (15–17). The rates of β-scission of exocyclic C–C bonds in alkyl group substituents with three or more carbon atoms are similar in magnitude to those of mono- and dibranched alkanes. In marked contrast, the rates of β-scission of endocyclic naphthene ring C–C bonds are two to three orders of magnitude slower (18). These differences in rates are responsible for the unacceptably low SRO yields over bifunctional hydrocracking catalysts, where the metal function is most often dominated by a strong acidity function, resulting in excessive naphthene side-chain and product alkane cracking (19, 20).

The third potential ring-opening pathway, which constitutes the central topic of this paper, is via metal-catalyzed hydrogenolysis. A voluminous literature has shown that ring opening methylcyclopentane to an isomeric mixture of C₆-alkanes can be accomplished with high selectivity over a number of supported Group VIII metals and metal alloys (21–25). Hydrogenolysis of alkyl-substituted naphthenes can occur by breaking either endocyclic or exocyclic C–C bonds. Rupture of a single endocyclic C–C bond in an alkylsubstituted one-ring naphthene leads to an alkane having the same carbon number. An example of such a SRO is the formation of *n*-decane from pentylcyclopentane. In contrast, breaking of an exocyclic C–C bond results in the loss of an alkyl substituent, or portion thereof, which decreases molecular weight by generating two lower molecular weight product molecules. Nonselective dealkylation is exemplified by the formation of ethylcyclopentane and propane from pentylcyclopentane. Nonselective ring opening also results when endocyclic and exocyclic C–C bonds are cleaved concurrently or consecutively. The formation of methane and *n*-nonane from *n*-pentylcyclopentane is another example of nonselective ring opening.

Petroleum distillates contain a complex mixture of five- and six-membered-ring naphthenes which often have multiple alkyl substituents and which may be joined to one another or fused to aromatic rings. Therefore, differences in ring-opening rates and selectivities between five- and six-membered-ring systems require quantification. Since ring structures in distillate feeds contain both short (one

TABLE 1
Comparison of Ring-Opening Pathways^a

Primary conversion route	Catalyst type	Naphthene ring/alkane (side chain) bond cleavage ratio
Free radical	None—thermal	<1.0
Carbocation	Solid acids	≪1.0
Hydrogenolysis	Metals	>1.0

^a Paraffin radical cracking rates are 5–50 times higher than that of naphthenic rings of equivalent carbon number. Acid cracking rates of alkanes and side chains on naphthenic rings are 10- to 1000-fold higher than naphthenic ring-opening rates. Ring-strain energies of approximately 1 and 7 kcal/mol, respectively, for six- and five-membered rings provide the rationale for why hydrogenolysis of naphthene rings is favored over alkane bond cleavage.

to two carbon atoms, as in cracked distillates) and longer (three carbon atoms and larger, as in virgin distillates) side chains, it is critically important to establish how the length, number, and ring position of side chains affect the ring-opening rates and selectivities of alkyl-substituted naphthenes.

3.2. Metal-Catalyzed Hydrogenolysis of Five-Membered-Ring Naphthenes

The hydrogenolysis patterns of methylcyclopentane (MCP) and *n*-pentylcyclopentane (PCP) are summarized in Table 2. All metal catalysts tested, with the exception of Ru, exhibited MCP ring-opening selectivities of 80% and higher. The much lower ring-opening selectivity displayed by Ru results from extensive secondary cracking of the primary C₆-alkane hydrogenolysis products to C₁-C₅ paraffins. The observed activity trend is in good agreement with a large literature reviewed in Ref. (26). Ring-opening selectivities for PCP tend to be somewhat lower than those of MCP but remain above 70% for Al₂O₃-supported platinum, ruthenium, rhodium, and iridium catalysts. Platinum is substantially less active than the other metal catalysts tested, requiring both higher reaction temperatures and lower space velocities (one-half for MCP to one-tenth for PCP) to reach comparable conversion levels. When considering the potential application of metal-based catalysts to SRO higher molecular weight alkylcyclopentanes such as *n*-pentylcyclopentane, iridium-based catalysts stand out as the most active and selective.

TABLE 2

Hydrogenolysis of Five-Membered-Ring Naphthenes

Feed	Catalyst	<i>T</i> (K)	Weight (%)			RO selectivity (%)
			Conversion	Cracking	RO ^a	
MCP ^b	0.6% Pt/SiO ₂	623	24.3	0.3	23.9	98
	0.3% Pt/Al ₂ O ₃	623	10.4	0.3	10.1	97
	15% Ni/Al ₂ O ₃	548	17.8	3.6	14.2	80
	1.5% Ru/SiO ₂	548	17.0	9.9	7.1	42
	0.9% Ir/Al ₂ O ₃	548	52.0	tr	52.0	99
PCP ^c	0.9% Pt/Al ₂ O ₃	573	91.0	19.1	61.9	68
	0.5% Ru/Al ₂ O ₃	498	44.0	7.9	36.1	82
	0.5% Rh/Al ₂ O ₃	548	68.3	8.9	59.4	87
	0.9% Ir/Al ₂ O ₃	523	65.0	5.2	59.8	92

Note. Isomerization of PCP to other C₁₀-naphthenes accounts for cases where cracking and ring-opening yields do not sum to percentage conversion.

^a Ring-opening yield MCP = wt% (*n*-hexane + 2-methylpentane + 3-methylpentane). Ring-opening yield PCP = wt% (*n*-decane + 4-methylnonane + 3-ethyloctane).

^b Methylcyclopentane, 2850 kPa; WHW = 15 for Pt and 30 for Ru, Ni, and Ir; H₂/MCP = 5.

^c 20% *n*-pentylcyclopentane/*n*-heptane; 3540 kPa; LHSV = 0.5 for Pt and 5 for Ru, Rh, and Ir; H₂/PCP = 15.

TABLE 3

Hydrogenolysis Product Distributions from Five-Membered-Ring Naphthenes Are Highly Metal Dependent

Feed	Products	Pt/Al ₂ O ₃ (%)	Multiplet ^a (%)	Ir/Al ₂ O ₃ (%)	Dicarbene ^a (%)
MCP	<i>n</i> -Hexane	41	40	<1	0
	2-Methylpentane	42	40	70	67
	3-Methylpentane	17	20	29	33
PCP	<i>n</i> -Decane	55	40	3	0
	4-Methylnonane	31	40	64	67
	3-Ethyloctane	14	20	33	33

Note. Conditions: Same as those given in Table 2.

^a Theoretical product distributions.

3.3. Hydrogenolysis Product Distributions from Five-Membered-Ring Naphthenes

Alkane product distributions resulting from the hydrogenolysis of MCP and PCP over well-dispersed (>90%) Pt/Al₂O₃ and Ir/Al₂O₃ catalysts are summarized in Table 3. Ring-opened product distributions for both MCP and PCP over Pt/Al₂O₃ are consistent with the multiplet mechanism (nonselective ring opening) proposed for the essentially statistical, endocyclic bond breaking of MCP over platinum catalysts (23). In the case of PCP hydrogenolysis, platinum displays a preference for bond cleavage at the tertiary carbon, as evidenced by a relatively high *n*-decane selectivity. For Ir/Al₂O₃, the ring-opened product distribution is substantially different and is in agreement with a dicarbene mechanism (selective ring opening) which preferentially induces endocyclic C-C bond breakage at unsubstituted C-C bonds (23). As predicted by the dicarbene mechanism, the relative quantities of *n*-hexane from MCP and *n*-decane from PCP are small and the 2-methylpentane-to-3-methylpentane and 4-methylnonane-to-3-ethyloctane product ratios are near the expected values of two. We have observed that the strong preference for secondary-secondary H₂C-CH₂ bond cleavage displayed by iridium is also exhibited by nickel, ruthenium, and rhodium hydrogenolysis catalysts.

3.4. Reactivity and Product Distribution Patterns from the Hydrogenolysis of Ethylcyclopentane and 1,1-, 1,2-, and 1-3-Dimethylcyclopentanes over Iridium and Platinum Catalysts

Since naphthenes in middistillate petroleum streams generally possess multiple substituents, it is imperative to understand the impact substitution patterns have on the ring-opening activities and selectivities of alkyl-substituted cyclopentanes. Four alkylcyclopentanes, each containing seven carbon atoms, namely ethylcyclopentane (ECP), 1,1-dimethylcyclopentane (1,1-DMCP),

TABLE 4
Ring-Opening Yields from ECP, 1,1-DMCP, 1,2-DMCP, and 1,3-DMCP over 0.9% Ir/Al₂O₃
Are Proportional to the Number of H₂C-CH₂ Ring Bonds

Compound	No. CH ₂ -CH ₂ bonds	% RO yield ^a	Alkane product distribution (%)						
			2-MeC ₆	3-MeC ₆	3-EtC ₅	2,4-DiMeC ₅	2,3-DiMeC ₅	2,2-DiMeC ₅	3,3-DiMeC ₅
ECP	3	56	—	66	34	—	—	—	—
1,3-DMCP	1	20	2	1	—	97	—	—	—
1,2-DMCP	2	31	—	2	—	—	98	—	—
1,1-DMCP	3	49	—	—	—	—	—	85	15

Note. Feed: 20 wt % alkylcyclopentane/80 wt % *n*-hexane. Conditions: 548 K, 3540 kPa, H₂/feed = 6, LHSV = 5.

^a % RO yield \cong percentage conversion as cracking and isomerization are limited.

1,2-dimethylcyclopentane (1,2-DMCP), and 1,3-dimethylcyclopentane (1,3-DMCP), were used to explore ring-substitution effects over both platinum and iridium catalysts and to determine whether well-dispersed platinum catalysts statistically cleave ring C-C bonds while well-dispersed iridium catalysts preferentially break unsubstituted ring C-C bonds. Table 4 summarizes the ring-opening yields and product distributions from the four cyclopentanes over a 0.9% Ir/Al₂O₃ catalyst. Ring-opening yields and relative ring-opening rates (run conditions were the same for each C₇-cyclopentane) are directly proportional to the number of unsubstituted H₂C-CH₂ ring bonds in each isomer. The observed alkane product distributions are, with the exception of those of 1,1-DMCP, in good agreement with those predicted (Fig. 3) by a dicarbene bond scission mechanism which assumes a perpendicular adsorption of five-membered rings onto the metal surface. This con-

jecture is supported by NEXAFS measurements carried out in laboratories which have shown that cyclopentene is bonded in a perpendicular orientation ($80 \pm 10^\circ$) to an Ir(111) single crystal.

For a 0.6% Pt/SiO₂ catalyst the ring-opening yields and rates are, in contrast, directly proportional to the concentration of *cis*-isomers in the individual dimethylcyclopentane reactant molecules (see Table 5). The product distributions are consistent with the multiplet mechanism. *Cis*-substitution of methyl groups allows "flat" adsorption of the five-membered ring onto the platinum surface, while *trans*-substitution severely hinders a planar adsorption (27). ECP with a single ring substituent is the most reactive of the C₇-cyclopentanes studied. 1,1-DMCP exhibits the lowest activity, presumably because flat adsorption is strongly inhibited. 1,3- and 1,2-DMCP display intermediate reactivities which are proportional to the level of *cis*-substitution in the starting feedstock. The concentrations of *cis*-substitution, as ascertained by GC measurements, are close to the thermodynamic values of 40 and 20%, respectively, for 1,3- and 1,2-DMCP at 600 K (28). The levels of *cis*-substitution in the product remain near equilibrium, indicating that *cis/trans* isomerization is fast relative to the ring-opening step. This observation is in agreement with a literature report (29). Alkane selectivities from C₇-alkylcyclopentanes do not follow a statistical distribution as closely as does MCP; however, trends are similar. The high yield of *n*-heptane arising from ethylcyclopentane ring opening suggests that substituents larger than methyl favor substituted C-C bond cleavage over platinum. As noted earlier, a similar preference for cleaving substituted C-C bonds was observed for *n*-pentylcyclopentane. The concentration of 2,3-dimethylpentane, which results from rupture of the two H₂C-CH₂ bonds in 1,2-dimethylcyclopentane, is unusually high, while the yield of 2,4-dimethylpentane which is formed by breaking the single H₂C-CH₂ bond in 1,3-dimethylcyclopentane is close to statistical. The basis for these differences in alkane product selectivities is not well understood.

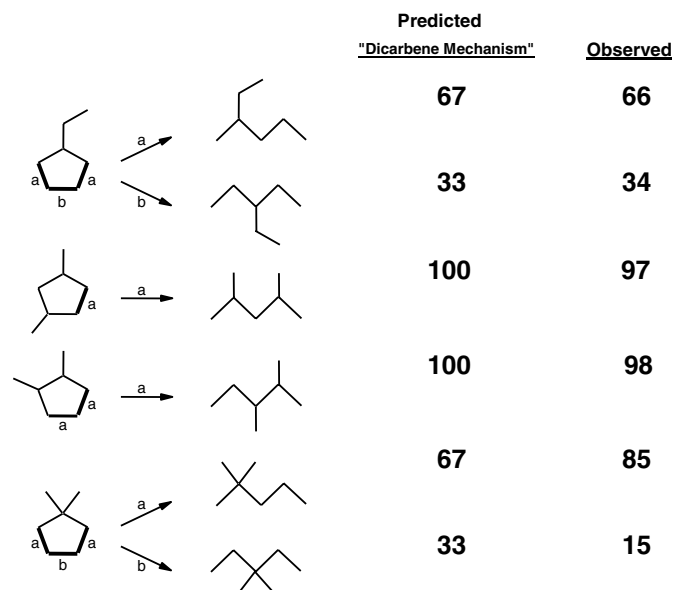


FIG. 3. Predicted and observed ring-opening product distributions from isomeric C₇-cyclopentanes over 0.9% Ir/Al₂O₃.

TABLE 5

Ring-Opening Yields from ECP, 1,1-DMCP, 1,2-DMCP, and 1,3-DMCP over 0.6% Pt/SiO₂ Are Proportional to *Cis*-Isomer Concentration

Compound	% <i>Cis</i> -isomer ^a	% RO yield ^b	Alkane product distribution (%)							
			<i>n</i> -C ₇	2-MeC ₆	3-MeC ₆	3-EtC ₅	2,4-DiMeC ₅	2,3-DiMeC ₅	2,2-DiMeC ₅	3,3-DiMeC ₅
ECP	N/A	34	54	—	28	18	—	—	—	—
1,3-DMCP	50	17	—	38	45	—	17	—	—	—
1,2-DMCP	20	9	9	—	29	—	—	62	—	—
1,1-DMCP	—	2	—	44	—	—	—	—	29	27

Note. Feed: 20 wt% alkylcyclopentane/80 wt% *n*-hexane. Conditions: 583 K, 3540 kPa, H₂/feed = 6, LHSV = 5.

^a Measured by GC.

^b % RO yield \cong percentage conversion as cracking and isomerization are limited.

3.5. Metal-Catalyzed Hydrogenolysis of Six-Membered-Ring Naphthenes

Hydrogenolysis reaction patterns for methylcyclohexane (MCH) and *n*-butylcyclohexane (BCH) over iridium, ruthenium, nickel, and platinum are summarized in Table 6. SRO is much slower for six-membered rings than five-membered rings for all metals examined. MCH reactivity patterns for these metals are similar to those found for methylcyclopentane, with one major exception. Platinum, which opens MCP with a 98% selectivity to C₆-alkanes, displays only a 4–5% selectivity for ring-opening MCH to C₇-alkanes. MCH ring-opening selectivities shown by nickel and ruthenium are also substantially lower than those obtained for MCP. Only iridium exhibited a high (87%) selectivity for directly opening the six-membered ring of MCH. Relative ring-opening activities as measured by ring-opening yields follow the same trend found for MCP. Actual activities, however, are much lower for MCH. For example, under the same space velocity and hydrogen partial pressure conditions, 0.9% Ir/Al₂O₃ converted, at 523 K, 52% MCP with a 99% selectivity to ring-opened products

(Table 2), while at 548 K the same catalyst exhibited a 14.5% conversion of methylcyclohexane with a 87% ring-opening selectivity. The significantly lower ring-opening selectivity reported in Table 6 for BCH when compared to MCH (35 vs 87%) for Ir/Al₂O₃ resulted from extensive hydrogenolysis of the butyl chain, not acid site dealkylation.

3.6. Hydrogenolysis Product Distributions from Methylcyclohexane

Iridium-, ruthenium-, and nickel-based catalysts preferentially break the unsubstituted H₂C–CH₂ bonds in MCH (Table 7). This observation is reasonably consistent with a dicarbene mechanism for both five- and six-membered rings. Similar observations have been reported for iridium and ruthenium (30, 31). *n*-Heptane is the major MCH ring-opening product over 0.6% Pt/SiO₂, with only trace amounts of 3-methylhexane formed. This is much different than a statistical distribution predicted by a multiplet mechanism, i.e., equal amounts of *n*-heptane, 2-methylhexane, and 3-methylhexane. This is not entirely surprising since “flat” adsorption of a cyclohexyl ring is not favorable.

TABLE 6

Hydrogenolysis of Six-Membered-Ring Naphthenes

Feed	Catalyst	<i>T</i> (K)	Weight (%)				RO selectivity (%)
			Conversion	Cracking	RO ^a	Aromatics	
MCH ^b	0.6% Pt/SiO ₂	623	5.5	1.7	0.2	3.4	4
	0.5% Pt/Al ₂ O ₃	623	6.6	0.1	0.3	5.9	5
	15% Ni/Al ₂ O ₃	548	2.3	1.9	0.3	0.1	12
	1.5% Ru/SiO ₂	548	52.9	50.2	2.1	0.5	4
	0.9% Ir/Al ₂ O ₃	548	14.5	1.9	12.6	tr	87
BCH ^c	0.9% Pt/Al ₂ O ₃	573	<1	<1	0	tr	0
	0.9% Ir/Al ₂ O ₃	548	38.4	22.0	13.6	2.6	35

^a RO yield MCP = wt% (*n*-heptane + 2-methylhexane + 3-methylhexane). RO yield BCH = wt% (*n*-decane + 5-methylnonane + 4-ethyloctane).

^b Methylcyclohexane, 2850 kPa; WHW = 5 for Ni, 15 for Pt, and 30 for Ru and Ir; H₂/MCH = 5.

^c 20% *n*-butylcyclohexane/*n*-heptane, 3540 kPa; WHW = 7 for Pt, 9 for Ir; H₂/BCH = 15.

TABLE 7

Representative Methylcyclohexane Hydrogenolysis Product Distributions

Catalyst	Alkane product distribution (%)		
	<i>n</i> -Heptane	2-Methylhexane	3-Methylhexane
0.6% Pt/SiO ₂	65	35	tr
15% Ni/Al ₂ O ₃	4	48	48
1.5% Ru/SiO ₂	13	38	49
0.9% Ir/Al ₂ O ₃	5	37	58

Note. Conditions: Same as those given in Table 6.

3.7. Competitive Conversion of Methylcyclopentane and Methylcyclohexane over Ir/Al₂O₃

Reaction rates extracted from the competitive conversion of MCP and MCH over a 2% Ir/Al₂O₃ catalyst are summarized in Table 8. At 523 K the ring-opening rate of MCP is at least sixfold higher than that of MCH even though MCH, because of its higher molecular weight, might be expected to be more strongly adsorbed and preferentially converted. Ring-opening selectivity is also much higher for MCP than MCH and the selectivity spread between these two molecules increases markedly with temperature as a result of an enhanced light gas make. The presence of substantially higher ring strain in five-membered- compared to six-membered-ring naphthenes, 6–7 vs about 1 kcal/mol, respectively, is assumed to be responsible for the higher hydrogenolysis rates exhibited by five-membered-ring naphthenes (32). The effect of ring conformation on adsorption may also be a contributing factor.

3.8. Conversion of Bicyclic Naphthenes Over Ir/Al₂O₃

The ease of converting two-ring naphthenes containing combinations of five- and six-membered rings over 0.9% Ir/Al₂O₃ is directly linked to the relative number of saturated five-membered rings in the molecule (see Table 9). Under the reaction conditions employed, perhydroindan containing one five-membered ring is more easily converted to mixture of single-ring alkylcyclohexanes than is

TABLE 8

Competitive Conversion of Methylcyclopentane and Methylcyclohexane over 2% Ir/Al₂O₃

<i>T</i> (K)	Rates (mol/h/kg)					
	Methylcyclopentane			Methylcyclohexane		
	C ₁ –C ₅	RO	Total	C ₁ –C ₆	RO	Total
523	tr	77	77	2	10	12
558	15	109	124	34	29	66

Note. Conditions: 2850 kPa; H₂/Feed = 5; WHW = 13 MCP, 17 MCH.

TABLE 9

Hydrogenolysis of Bicyclic Naphthenic Molecules over 0.9% Ir/Al₂O₃

Molecule	<i>T</i> (K)	Conversion	Product distribution (%)	
			1-Ring naphthene	Acyclic paraffins
Decalin	548	4.4	4	tr
Perhydroindan	548	68	56	tr
Bicyclo[3,3,0]octane	498	81	60	21
Bicyclo[3,3,0]octane ^a	498	99	17	82

Note. Conditions: 3540 kPa, LHSV = 1.6, 2000 SCF H₂/BBL.

^aLHSV = 0.8.

decalin, which has only six-membered rings. In marked contrast, bicyclo[3,3,0]octane, containing two saturated five-membered rings, is selectively and completely (82% at 99% conversion) ring opened to C₈-alkanes.

3.9. Ring Opening of 1,2,4-Trimethylcyclohexane Over Ir/Al₂O₃

Hydrogenolysis of 1,2,4-trimethylcyclohexane (1,2,4-TMCH) over 0.9% Ir/Al₂O₃ was investigated to explore a number of important issues, namely activity, selectivity, and product distribution patterns associated with ring opening multiply substituted cyclohexanes. As expected from our studies of DMCPs, the reactivity of 1,2,4-TMCH is markedly lower than that of MCH (see Table 10). MCH conversion at 573 K is roughly twice that of 1,2,4-TMCH at 10 times the liquid hourly space velocity. Increasing the number of substituents from one to three on six-membered rings not only drastically lowers ring reactivity, it also reduces appreciably ring-opening selectivity. SRO of 1,2,4-TMCH can result in the generation of six isomeric nonanes (see Fig. 4 and Table 11). Cleavage of the single unsubstituted H₂C–CH₂ bond in 1,2,4-TMCH leading to the formation of 2,3,5-trimethylhexane accounts for only 30–40% of the C₉-alkanes produced despite the established preference of iridium for breaking unsubstituted H₂C–CH₂ ring

TABLE 10

1,2,4-Trimethylcyclohexane Is Significantly More Difficult to Ring Open than Methylcyclohexane

	<i>T</i> (K)	% Conversion	Ring-opening yield (%)	Ring-opening selectivity (%)
1,2,4-TMCH	548	12.7	5.1	40
	573	42.0	16.7	40
MCH	573	73.2	52.7	72

Note. Catalyst: 0.9% Ir/Al₂O₃. Conditions: 3540 kPa, 1 LHSV, and H₂/feed = 6 for 1,2,4-TMCH; 2850 kPa, 10.5 LHSV, and H₂/feed = 6 for MCH.

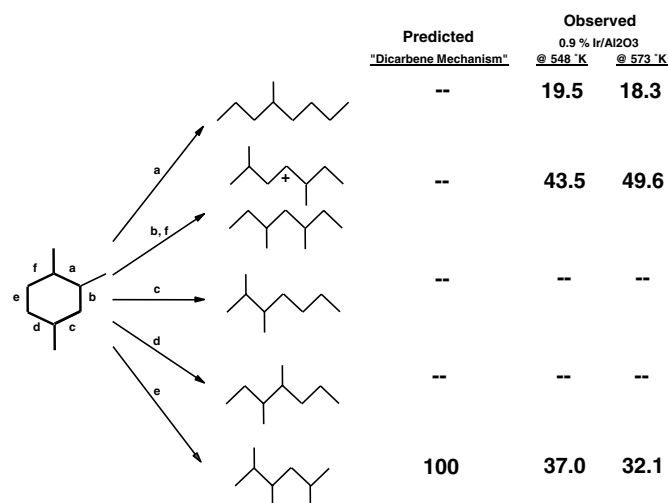


FIG. 4. Predicted and observed ring-opening product distribution from 1,2,4-trimethylcyclohexane over 0.9% Ir/Al₂O₃.

bonds. Cleavage of the most sterically hindered ring C–C bond yields 4-methyloctane, which makes up about 20% of the product C₉–alkanes. 2,5- and 3,5-dimethylheptanes, which are not resolved by our GC equipment, together account for 45–50% of the product C₉–alkanes. Of the C₉–alkanes generated over 0.9% Ir/Al₂O₃ 60–70% of them result from breaking of mono- or disubstituted ring C–C bonds. The ability of iridium to cleave substituted C–C bonds was not anticipated, based upon the behavior of all the other five- and six-membered-ring naphthenes examined in this study. The high selectivity shown for C₉–alkanes resulting from substituted bond cleavage of 1,2,4-TMCH indicates that a change in mechanism occurs during the direct cleavage of highly substituted cyclohexane rings. The possibility that the methyl groups themselves function as reaction centers is suggested. For example, metallacyclopentane and/or mono- and dicarbene species may result via interaction of exocyclic methyl groups with the metal surface. The involvement of such species was suggested in the rupture of the highly hindered quaternary C–C bond in 2,2,3,3-tetramethylbutane over ruthenium, a metal similar in reactivity pattern to iridium (33).

TABLE 11

Iridium Displays Unusual Selectivities for Ring Opening
1,2,4-Trimethylcyclohexane

T (K)	Alkane product distribution (%)				
	4-MeC ₈	3,5- + 2,5-DiMeC ₇	2,3-DiMeC ₇	3,4-DiMeC ₇	2,3,5-TriMeC ₆
548	19.5	43.5	—	—	37.0
573	18.3	49.6	—	—	32.1

Note. Conditions: Same as those given in Table 10.

3.10. The Importance of Acidity in Selective Ring Opening of Six-Membered-Ring Naphthenes

Reaction chemistry information discussed so far indicates that hydrogenolysis over metals, and in particular over iridium, can be used to convert five-membered-ring naphthenes into alkanes without significant loss in molecular weight. A modified approach, however, is needed to selectively ring-open six-membered-ring naphthenes. A potential route is the use of metal-and-acid-balanced bifunctional catalysts to isomerize six-membered-ring naphthenes to five-membered-ring naphthenes prior to ring opening. It was also shown that increased ring substitution lowers ring-opening yields and increases the production of highly branched, lower cetane number alkanes. To limit the branchiness of the product alkanes an acidic C₆- to C₅-ring-contraction function which minimizes the number of ring substituents and also minimizes secondary skeletal isomerization of product alkanes is desired. A much simplified reaction network for ring-opening MCH, including C₆- to C₅-ring contraction and subsequent hydrogenolysis of C₅-rings, is illustrated in Fig. 5. Nonbranching ring contraction to ECP followed by ring opening is the preferred path because higher ring-opening rates and less branched alkane products are possible with this isomer. Branching isomerization of MCH to DMCPs is undesirable since subsequent ring opening would be retarded and product C₇–alkanes would tend to be more highly branched. Direct ring opening of MCH is the least favored path, as both ring cleavage rates and selectivities are low. Table 12 highlights typical variations in overall conversion rates and selectivities for nonbranching ring contraction (ECP formation) over representative platinum-loaded amorphous and crystalline solid acids. Ring-contraction rates, which account for over 95% of the total conversion rates under the conditions employed, are directly related to the relative number of effective acid sites, which in the case of microporous crystalline solid acids reflects complex changes in structure, Si/Al ratio, and elemental composition, while ECP selectivities at a given conversion level provide information

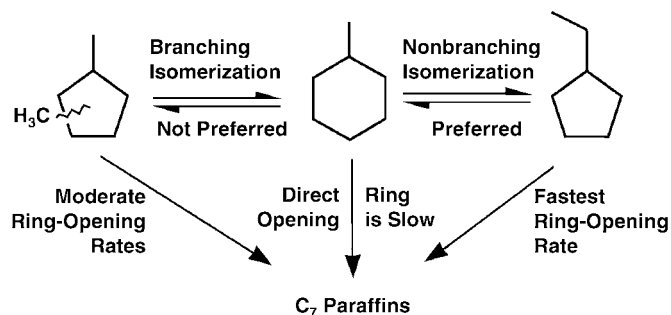


FIG. 5. Nonbranching isomerization of MCH to ECP prior to ring opening is preferred over either direct MCH ring opening or cleaving dimethyl-substituted cyclopentane rings.

TABLE 12

Moderate Acidity Favors Nonbranching Ring Contraction of Methylcyclohexane

Catalyst (0.5% Pt)	Si/Al	Ring-contraction rate ^a	% ECP at 20%
			conv.
Pt/Al ₂ O ₃	—	0.05	—
Pt/SiO ₂ -Al ₂ O ₃	3.4	1.3	42
Pt/SAPO-11	0.05	4.2	45
Pt/ECR-32	66	40.0	44
Pt/USY	37	25.3	38
Pt/USY	8.3	105	33
Pt/LZY-82	5.1	132	26
Pt/beta	15	126	17
		Equilibrium values ^b	9–11

Note. Conditions: WHW = 15, H₂/MCH = 5, 2850 kPa, 548–598 K.

^a Rates in mol/h/g × 1000, at 548 K.

^b Over the temperature range 548–598 K.

on relative differences in acid strength (34). High ECP selectivities, indicating low-to-moderate acid strengths, are observed for amorphous SiO₂/Al₂O₃, highly dealuminated USY and ECR-32 zeolites (35), and microporous materials such as SAPO-11. Lower ECP selectivities, which reflect a closer approach to equilibrium, are displayed by higher acid strength materials such as LZY-82, a typical catalytic cracking catalyst, and zeolite beta.

A significant increase in MCH ring-opening yield and rate is achieved upon either staging or admixing a moderate-acidity ring-contraction catalyst, 0.9% Pt/USY (Si/Al = 37), with a 2% Ir/Al₂O₃ hydrogenolysis catalyst (see Table 13). The acidic Pt/USY catalyst by itself is not active for ring opening but effectively catalyzes ring contraction (RC), as noted by a high RC selectivity near 98%. Addition of two parts by weight of the Pt/USY ring-contraction catalyst to one part by weight of Ir/Al₂O₃ doubled the ring-opening yield and halved the cracking yield of

TABLE 13

Methylcyclohexane Ring Opening Is Enhanced by Addition of an Acidic Ring Contraction Catalyst to an Ir/Al₂O₃ Hydrogenolysis Catalyst

Catalyst	Weight (%)				RO selectivity (%)
	Conv.	Cracking	RO	RC	
2% Ir/Al ₂ O ₃	24.8	6.4	18.1	0.3	73
0.9% Pt/USY(Si/Al = 37)	9.3	0.2	tr	9.1	<0.1
0.9% Pt/USY(Si/Al = 37) ^a followed by 2% Ir/Al ₂ O ₃	51.0	2.6	34.2	13.8	67
0.9% Pt/USY(Si/Al = 37) ^a admixed with 2% Ir/Al ₂ O ₃	55.0	2.8	38.5	13.7	70

Note. Conditions: steady-state activities; 548 K; 2850 kPa; WHW = 15 for Pt/USY and 30 for Ir catalysts.

^a Two parts Pt/USY, one part Ir/Al₂O₃.

TABLE 14

Methylcyclohexane Ring Opening Patterns of 0.9% Iridium on ECR-32 Supports of Varying Acidities^a

Si/Al	% Conv.	Rates (mol/h/kg)				
		C ₁ -C ₆	RO	RC	Total	% RO
12	35.8	2.04	20.4	89.5	112	18
51	27.9	1.63	32.1	53.7	87.5	37
66	17.6	2.19	32.3	20.5	55.0	59
95	9.72	1.87	20.5	7.87	30.5	67
200	6.84	2.69	18.5	—	21.5	86

Note. Conditions: 0.5 g catalyst; 20 cm³ MCH/h; 2850 kPa; H₂/MCH = 5.0; 548 K.

^a ECR-32 supports are USY materials.

the iridium-only catalyst. The acidic ring-contraction component was found to be equally efficient whether staged upstream of or physically admixed, as 10/20 mesh particles, with the 2% iridium ring-opening catalyst.

A systematic study of 0.9% Ir on a series of ECR-32 zeolitic (USY materials) supports was undertaken to better define the role metal/acid balance plays in the selective ring opening of MCH (36). As synthesized ECR-32 zeolites have Si/Al ratios near 6. Higher Si/Al ratio materials were prepared by steam calcination followed by acid washing with various HCl concentrations. The details of preparation and characterization of ECR-32 materials are reported elsewhere (35). As seen in Table 14 ring-opening selectivity increases with the Si/Al ratio whereas the apparent ring-opening rate goes through a maximum between Si/Al ratios of 50 and 70. The best compromise for ECR-32-based catalysts is obtained with materials having Si/Al ratios between 50 and 100, where relatively high ring-opening selectivities are achieved without a significant debit in ring-opening rates.

The effect of acidity on the ring-opening patterns of *n*-pentylcyclopentane (PCP) and *n*-butylcyclohexane (BCH) over both platinum- and iridium-based catalysts is summarized in Table 15. In the case of PCP ring opening, supporting iridium on a moderate acidity USY with a Si/Al mole ratio near 37 significantly decreases both ring-opening yield and selectivity compared to iridium on a much lower acidity Al₂O₃ carrier. The major PCP reaction products over moderately acidic platinum and iridium catalysts are a complex mixture of C₁₀-cyclohexanes and C₁₀-cyclopentanes, most of which have multiple alkyl substituents. Addition of a moderate acidic function results, then, in enhanced isomerization activity, which includes consecutive ring expansions and contractions, as well as redistribution of exocyclic side chains forming multiple alkyl substituents. The consequence of acidity-catalyzed isomerization of PCP is a large decrease in the number of reactive C-C bonds. Acidity function enhancement

TABLE 15

Effect of Acidity on the Ring Opening of *n*-Pentylcyclopentane and *n*-Butylcyclohexane over Platinum and Iridium

Feed	Catalyst	<i>T</i> (K)	Weight (%)				RO selectivity (%)
			Conversion	Cracking	RO	Isomerization	
PCP	0.9% Pt/Al ₂ O ₃	573	5	0.6	3.7	0.8	74
	0.9% Ir/Al ₂ O ₃	523	65	5	60	tr	92
	0.9% Pt/USY (37)	548	92	14	4.5	73	5
	0.9% Ir/USY (37)	523	96	8	30	58	31
BCH	0.9% Ir/Al ₂ O ₃	548	38	22	14	<1	35
	0.9% Ir/Al ₂ O ₃ ^a	548	69	16	30	23	43
	+ 0.9% Pt/USY (37)						
	0.9% Ir/Al ₂ O ₃ ^b	548	70	10	10	50	14
	+ 0.9% Pt/USY (37)						
	0.9% Ir/USY (37)	548	83	9	14	60	17
0.9% Pt/USY (37)	548	85	15	0	70	0	

Note. Conditions: 20% *n*-pentylcyclopentane or *n*-butylcyclohexane in *n*-heptane; 3540 kPa; LHSV = 5; H₂/PCP or BCH = 15.

^a Five parts Ir/Al₂O₃, one part Pt/USY.

^b Five parts Ir/Al₂O₃, three parts Pt/USY.

reduces the PCP ring-opening yield over iridium from 60 to 30 wt%.

As found for MCH, converting BCH over an admixed catalyst system comprised of one part acidic Pt/USY(37) catalyst and five parts Ir/Al₂O₃ hydrogenolysis catalyst increased the ring-opening yield from 14 to 30%. Increasing the amount of Pt/USY(37) threefold, however, resulted in a decrease in ring-opening yield from 14 to 10% vs. that with the Ir-only catalyst. Upping the relative quantity of admixed Pt/USY(37) increases the number of effective isomerization sites, which transforms BCH more deeply into less reactive, multibranched five- and six-membered-ring naphthenes. The large ring-opening yield and selectivity differences exhibited by the 5 : 1 and 5 : 3 metal-to-acid admixtures clearly illustrates the important role metal/acid site balance plays in selective ring-opening chemistry. The addition of Pt/USY(37) to Ir/Al₂O₃ does not lower the cracking yield from BCH as found for MCH. The C₁–C₄ light gas

make from BCH is composed primarily of C₃ and C₄ paraffins, indicative of acid site cracking. Increased acid cracking of the butyl side chain of BCH explains in large part the cracking yield differences observed for BCH and MCH, as methyl groups are not easily cleaved by an acid-catalyzed route.

A bifunctional 0.9% Ir/USY(37), prepared by impregnating iridium directly onto an acidic USY(37) support, is a less active and selective ring-opening catalyst than an admixture of 0.9% Ir/Al₂O₃ plus 0.9% Pt/USY (37). The superior performance demonstrated by the physically mixed catalyst system results in the main from iridium being more highly dispersed on Al₂O₃ than on USY (37).

In the presence of an isomerization catalyst, the distribution of C₁₀ acyclic paraffins obtained from ring-opening BCH would be expected to differ greatly from that obtained from PCP. Di- and trisubstituted C₁₀–alkanes should be generated. Surprisingly, 4-methylnonane and 3-ethyloctane,

TABLE 16

C₁₀ Paraffin Distributions Suggest *n*-Pentylcyclopentane Is an Intermediate in *n*-Butylcyclohexane Ring Opening over Iridium/Acid Catalyst Systems

Catalyst	Feed	Alkane product distribution (%)						
		4-MeC ₉	3-EtC ₈	<i>n</i> -C ₁₀	5-MeC ₉	4-EtC ₈	3-MeC ₉	Other
0.9% Ir/Al ₂ O ₃	PCP	64	33	3	—	—	—	—
0.9% Ir/Al ₂ O ₃	BCH	—	—	6	34	60	—	—
0.9% Ir/Al ₂ O ₃ ^a	BCH	48	10	2	—	13	16	12
+ 0.9% Pt/USY (37)								
0.9% Ir/USY (37)	BCH	66	14	1	—	10	11	—

Note. Conditions: 20% *n*-pentylcyclopentane or *n*-butylcyclohexane in *n*-heptane; 3540 kPa; LHSV = 5; H₂/PCP or BCH = 15.

^a Five parts Ir/Al₂O₃, one part Pt/USY.

the primary products of direct PCP ring opening, are the major ring-opening products from BCH ring opening over the Ir/isomerization catalyst systems (Table 16). This suggests that PCP may be a principal intermediate in the selective ring opening of BCH. In an analogy to MCH ring contraction to ECP, PCP could form BCH via a nonbranching rearrangement. 4-Ethyl octane, which accounts for about 10% of the C₁₀-alkanes generated over moderately acidified iridium ring-opening catalysts, is not a direct, primary BCH conversion product, as no 5-methylnonane is coproduced. 4-Ethyl octane and 3-methylnonane likely result from secondary isomerization of 3-ethyl octane and 4-methylnonane, respectively.

4. CONCLUSIONS

Selective ring opening of naphthenic rings is a metals-driven chemistry. Iridium was found to be the most active and selective metal for cleaving unsubstituted C–C bonds in five-membered-ring naphthenes such as MCH and PCP. Ring-opening rates over iridium decrease significantly with the extent of alkyl group substitution and are directly proportional to the number of secondary–secondary H₂C–CH₂ bonds. Ruthenium, rhodium, and nickel exhibit a similar preference for cleaving unsubstituted ring C–C bonds, but these metals are generally less selective than iridium. Platinum is much less active for opening five-membered-rings than iridium but is better able to break substituted ring C–C bonds, leading to an approximately statistical alkane distribution. Two presumed mechanisms were invoked to explain the differences shown between iridium (nonstatistical) and platinum Pt (statistical) ring-opening product distributions from five-membered-ring naphthenes. A dicarbene mechanism is proposed for iridium in which cyclopentyl rings are assumed to bond perpendicularly to the iridium surface. In contrast, platinum-catalyzed hydrogenolysis of naphthene rings is proposed as proceeding by a “flat” (or parallel) adsorption of the cyclopentyl ring onto the metal surface, which allows simultaneous interaction with all ring C–C bonds (multiplet mechanism). Experiments carried out over dimethylcyclopentanes provided further evidence for the operation of these two different ring-opening mechanisms. Ring-opening rates over iridium are directly proportional to the number of unsubstituted, unencumbered H₂C–CH₂ bonds and markedly decrease with increasing ring substitution. The “flat” adsorption of *trans*-substituted cyclopentyl rings is inhibited on platinum surfaces; thus, ring-opening rates over platinum are sensitive to the *cis/trans* ratio of the isomeric dimethylcyclopentanes, decreasing with increasing *trans*-isomer concentration.

As found for five-membered-ring naphthenes, iridium is the most active and selective metal for the direct ring opening of six-membered-ring naphthenes and preferen-

tially breaks secondary–secondary H₂C–CH₂ bonds. Direct ring opening of a cyclohexyl ring is, however, much slower and substantially less selective than that of a cyclopentyl ring. Controlled isomerization of six-membered-ring naphthenes to five-membered-ring naphthenes provides a pathway for improving ring-opening rates (yields) and selectivities. Nonbranching ring contraction is the preferred isomerization route, as the number of ring substituents is minimized, enabling higher ring-opening rates and the formation of alkanes with fewer branches. Branching isomerization, including both side-chain and ring-contraction isomerizations to multisubstituted five-membered rings, must be avoided if high ring-opening rates and minimally branched alkane products are to be obtained. Both the acidity level of the ring-contraction function and the metal/acid balance are controllable catalyst properties which allow maximization of ring-opening rates and product selectivities and minimization of undesired hydrocracking and secondary acyclic paraffin isomerization reactions.

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