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# Paraffin Dehydrocyclization

## Distribution of Aromatic Products Obtained with "Nonacidic" Supported Pt Catalysts

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The distribution of the isomeric aromatic products from the dehydrocyclization of ten $C_8$–$C_9$ paraffins over a 0.6% Pt catalyst supported on "nonacidic" alumina has been determined. The aromatic isomers obtained experimentally are those predicted for a direct cyclization to the six-membered ring structure. The participation of other size ring intermediates recently proposed to explain dehydrocyclization over chromia is not required to explain our results with a platinum catalyst. The very small amount of aromatic isomers not expected from direct six-membered ring formation probably arise from dual functional catalytic isomerization of the reactant prior to cyclization. The aromatic product distribution suggests that a "geminal dialkylcyclohexane intermediate" contributes to the reaction pathway when such structures are allowed by a six-membered ring closure.

### INTRODUCTION

The mechanism for the formation of aromatics from paraffins—dehydrocyclization—has been the subject of numerous investigations. The literature to the early 1950's was reviewed by Hansch (*1*), Steiner (*2*), and Haensel (*3*). Pines and Goetschel (*4*) discussed the more recent literature for the mechanism of the aromatization of alkanes in the presence of chromia–alumina catalysts. Most of the literature concerning the mechanism of aromatization was directed toward learning: (a) whether the major reaction products, olefins and aromatics, are formed by a consecutive or a parallel reaction sequence, (b) whether the cyclization proceeded through a six-carbon ring intermediate only or whether ring intermediates of various carbon numbers were involved, (c) the relative rates of conversion of various normal and iso-paraffins, and (d) the relative amounts of the aromatic products.

The early proposal (*1–4*) that cyclization occurred via a six-carbon ring intermediate gained wide acceptance. However, in 1959, Kazanskii and Lieberman (*5*) proposed that, for Pt/C catalysts, the use of the term "dehydrocyclization" to cannote formation of 6-membered rings *only* from open chain hydrocarbons should be abandoned. They suggested that a more accurate terminology should include expressions for *both* $C_5$- and $C_6$-dehydrocyclization pathways. On the other hand, Kazanskii and coworkers (*6, 7*) implied that cyclization occurred by formation of six-membered rings over chromia–alumina catalysts; they also concluded that aromatic products not predicted by direct six-membered ring formation resulted from isomerization of the reactant carbon skeleton prior to cyclization.

Fogelberg *et al.* (*8*) recently reported the dehydrocyclization of $C_8$-paraffins using a low activity Pt–$Al_2O_3$—the alumina had been calcined at 1200°C to reduce the surface area and presumably the acidity. They also postulated intervention of six-membered ring intermediates, and attributed the diverse composition of the aromatic fraction obtained with more active catalyst samples to isomerization prior to ring closure.

Studies using $^{14}$C-labeled paraffins have been inconclusive for clearly defining whether six-carbon rings only or intermediates involving several rings of different size are involved in dehydrocyclization reaction pathways. Wheatcroft (*9*), using 1-heptene-1-$^{14}$C and a $Cr_2O_3$–$Al_2O_3$ catalyst, believed he had demonstrated cyclization to six-membered rings. Later, Mitchell (*10*) obtained results with *n*-heptane-1-$^{14}$C which were not compatible with direct six-membered ring formation. Pines and Chen (*11*) concluded that the formation to toluene, from *n*-heptane-1-$^{14}$C, may involve five-, six-, and seven-membered ring intermediates, the relative contribution depending on the nature of the catalyst and the time on stream. With both chromia and an acidic chromia–alumina, the six-membered ring intermediate predominated. However, with the less acidic potassium promoted chromia–alumina, they proposed that nearly all of the toluene resulted from a seven-membered ring intermediate which was free to "roll-around" on the surface to yield $^{14}$C equivalence at all positions in the toluene product. It should be emphasized that Pines and co-workers found the most $^{14}$C scrambling with the less acidic chromia–alumina; this would make it difficult to explain the isotope scrambling by a dual functional pathway involving an acidic isomerization. Pines and Gotschel (*12*) obtained similar results with several other $^{14}$C labeled hydrocarbons. Feighan and Davis (*13*) studied the dehydrocyclization of *n*-heptane-4-$^{14}$C over chromia, acidic chromia–alumina, and a less acidic potassium promoted chromia–alumina—catalysts similar to those used by Pines and co-workers —and obtained results which were compatible with direct six-membered ring formation with a small amount of side reactions leading to $^{14}$C scrambling. Furthermore, Feighan and Davis (*13*) found the largest amount of scrambling for the *unsupported* chromia catalyst.

The majority of the dehydrocyclization studies have been done with chromia or chromia–alumina catalyst. While the dehydrocyclization of many of the individual hydrocarbons was studied previously, a systematic comparison of the aromatic product distributions from the paraffins would involve results obtained over several different catalysts. Nearly all of the results published to date do not strictly conform to a mechanism involving *only* six-membered rings.

We have determined the aromatics formed by the dehydrocyclization of ten $C_8$ and $C_9$ paraffins using a Pt–$Al_2O_3$ catalyst. The alumina support was "nonacidic" (*14*); in addition, the chlorine added during impregnation was removed by washing with $NH_4OH$. The use of this catalyst system reduces the uncertainty as to the role of acidity associated with an oxide dehydrogenation component. In addition, the Pt–$Al_2O_3$ catalyst is more active so the dehydrocyclization reaction may be accomplished at a temperature 25–50°C lower than is required for the chromia catalyst; the lower temperature substantially reduces competing side reactions. Finally, the use of gas chromatographic analysis resulted in a more accurate determination of the aromatic product distribution than was possible in many of the early studies.

## EXPERIMENTAL METHODS

The simple flow apparatus consisted of a motor-driven syringe for liquid feed, a Vycor glass reaction tube wound with nichrome heater wire and fitted with a thermocouple well, a water cooled condenser, liquid collector, and gas flow meters. A preheater section (30 ml of 8–14 mesh quartz chips) preceded the catalyst bed (5 ml), which was held in place by quartz wool.

### *Catalysts*

**$Al_2O_3$–K.** This "nonacidic" alumina was prepared by the method of Pines and Chen (*11*). The alumina was mostly β-trihydrate after drying at 120°C; after calcination at 550°C it was mostly η-alumina. The alumina had an area of 200 $m^2/g$ after calcination at 600°C and contained 0.5 wt % potassium.

**$Al_2O_3$Li.** This alumina was prepared using the same procedure and molar ratios as used for $Al_2O_3$–K. However, lithium aluminate is insoluble whereas potassium aluminate is soluble. The insoluble lithium aluminate was washed with water to reduce the lithium content to 5.5 wt % ($LiAlO_2$ = 10.5 wt % Li). The surface area was 111 $m^2/g$ after calcination at 550°C for 6 hr. X-Ray analysis showed that crystalline $LiAlO_2$ was present in the calcined material.

**Pt-$Al_2O_3$–K, –Li.** The supported Pt catalysts were prepared by impregnation with just sufficient solution to "wet" the alumina. Thus, the necessary amount of chloroplatinic acid to give the desired metal content was added to just enough water to fill the alumina pore volume. The solution was added dropwise and the catalyst was allowed to stand 24 hr (*15*). The catalyst was then dried at 120°C.

The metal–alumina catalyst, which had been dried at 120°C, was heated to 230°C in a stream of nitrogen, then treated for 2 hr at 230°C with hydrogen, the temperature was increased to 510°C and maintained at this temperature for 2 hr in a flow of hydrogen; the catalyst was then purged with nitrogen at 510°C and cooled to room temperature. Portions of the *reduced* metal–alumina catalysts were then washed with a solution containing ca. 2% $NH_3$ to reduce the chlorine content to a low level. The Pt metal content is given in the text for the various Pt–alumina catalysts.

**Pt–$SiO_2$ catalyst.** Davidson Grade No. 62 silica was impregnated with an aqueous solution of chloroplatinic acid to give a catalyst containing 0.6% Pt.

**Hydrocarbons.** The hydrocarbons (all 99%+ purity) were obtained from Chemical Samples Company except for the following: *n*-octane, octene, and *n*-nonane, all pure grade from Phillips; 2,5-dimethyl-2,4-hexadiene, white label grade, Eastman Chemical; 2- and 3-methylheptane and 2,5-dimethylhexane from Aldrich Chemical. All hydrocarbons were used without further purification.

### *Methods*

The dehydrocyclization catalysts were reduced *in situ* by heating to 550°C in $H_2$ during a period of 15–20 min. The catalysts were held at 550°C for 3 hr in $H_2$ and then cooled to the reaction temperature in a hydrogen flow. The hydrocarbon flow of 1.5 ml/hr was started and hydrogen flow was stopped. All runs were made at atmospheric pressure with no added carrier gas. The reaction temperature was 482°C for all runs. Samples were usually taken after 0.4 ml of liquid was collected and thereafter as each 1.0 ml of liquid accumulated. A typical run lasted about 4 hr.

Analyses were made by gas chromatography using a 16 ft, ¼ in. column packed with 5% Bentone 34 and 5% diisodecylphthalate on Diataport W. The column was held at 100°C for 16 min and then the temperature was increased to 150°C at 10°/min. Helium carrier gas flow rate was 40 ml/min. The only difficulty encountered with the use of this column was the overlap of the isopropylbenzene: *o*-xylene peaks and 1,2,3-trimethylbenzene–indane peaks. All other $C_6$–$C_9$ aromatics encountered in this study were separated sufficiently to obtain reproducible quantitative analyses. The aromatic distributions are probably accurate to ±5% of the value reported except for the minor products (~5% yield or less). Total conversions are much less accurate because of the large number of minor liquid products, coke and gaseous products.

## RESULTS

The aromatic product distribution is plotted vs. the time on stream (beginning when the hydrocarbon flow was started). The points in the Figs. 1–7 are an average composition of each liquid sample collected (see "Experimental Methods" section). In all cases, we have compared our experimental results to those products expected for direct 1,6-ring closure of the reactant paraffin (inserts in Figs. 1–7).

Results for the dehydrocyclization of *n*-octane are shown in Fig. 1. More than 95% of the $C_8$ aromatic products are those allowed by direct 1,6-ring closure. The other two $C_8$ aromatic isomers, *m*- and *p*-xylene, are present in small amounts; in addition, the amounts of these two isomers

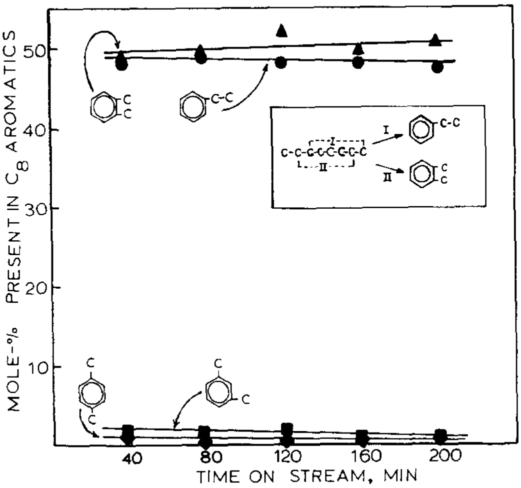


FIG. 1. Product distributions in the liquid $C_8$-aromatic fraction from the dehydrocyclization of *n*-octane over $Pt–Al_2O_3–K$.

decrease with time on stream. The expected isomers, ethylbenzene and *o*-xylene, are formed in equal amounts. Similar results for the $C_8$ aromatic isomer distribution were obtained with the $Pt–SiO_2$ and $Pt–Al_2O_3–Li$ catalysts.

The products obtained for the dehydrocyclization of 1-octene, 2-octene, and *trans*-4-octene are similar to those for *n*-octane; again 95% or more of the $C_8$-aromatic products are those expected for 1,6-ring closure. However, the relative amounts of ethylbenzene and *o*-xylene formed varied.

Results for 2- and 3-methylheptane are presented in Fig. 2. The products for 3-methylheptane dehydrocyclization are those expected for 1,6-ring closure; less than 5% of *m*-xylene, not allowed by 1,6-ring closure, is formed initially and this amount decreases with time on stream. As shown in the insert in Fig. 2, two $C_8$-aromatic isomer—*o*- and *p*-xylene—may be formed by nearly identical 1,6-ring closure pathways. However, the pathway leading to the less sterically hindered isomer, *p*-xylene, is apparently favored by a factor of 2. The formation of ethylbenzene by 1,6-ring closure must involve two $–CH_3$ groups whereas the other two pathways involves one $–CH_3$ and one $–CH_2–$ group. Apparently, the pathway involving two $–CH_3$ groups is a less favored pathway.

For 2-methylheptane, *m*-xylene is the only $C_8$-aromatic isomer allowed by direct 1,6-ring closure. *m*-Xylene is by far the major product; furthermore the other $C_8$-isomers are present in ratios similar to those expected for 3-methylheptane. As shown in the insert, there is a direct 1,6-ring closure than cannot lead directly to an aromatic by dehydrogenation. This ring closure pathway yields what may be formally regarded as adsorbed 1,1-dimethyl-

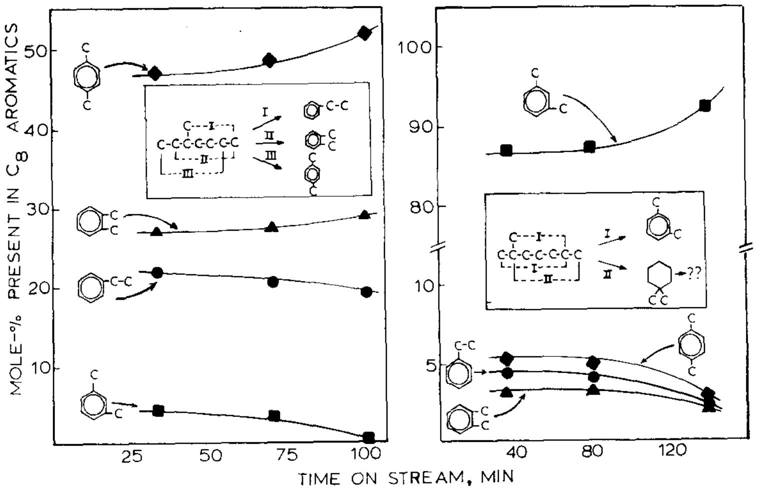


FIG. 2. Product distributions in the liquid $C_8$-aromatic fraction from the dehydrocyclization of 2- and 3-methylheptane over $Pt–Al_2O_3–K$.

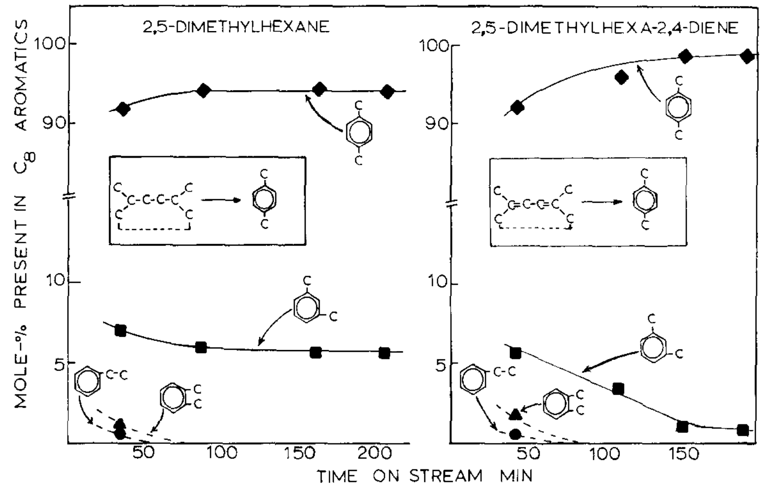


FIG. 3. Product distributions in the liquid $C_8$-aromatic fraction from the dehydrocyclization of 2,5-dimethylhexane and 2,5-dimethylhexa-2,4-diene over Pt–$Al_2O_3$–K.

cyclohexane—a geminal dialkylcyclohexane intermediate. For equivalent conversion to aromatics, 2-methylheptane produced more than twice as much toluene as 3-methylheptane and *n*-octane.

Results for the dehydrocyclization of three dimethylhexanes and 2,5-dimethyl-2,4-hexadiene are shown in Figs. 3 and 4. The major $C_8$-aromatic products obtained for 2,5-dimethylhexane, 2,5-dimethyl-2,4-hexadiene, and 2,4-dimethylhexane are those expected for direct 1,6-ring closure. The minor $C_8$-aromatic products for these three hydrocarbons may be explained by 1,2-methyl migrations of the reactants. For example, the predominate minor product for 2,5-dimethylhexane cyclization is *m*-xylene—the aromatic which would be formed as a result of a 1,2-methyl migration in the reactant paraffin prior to or during cyclization.

The major product formed from 3,4-di-

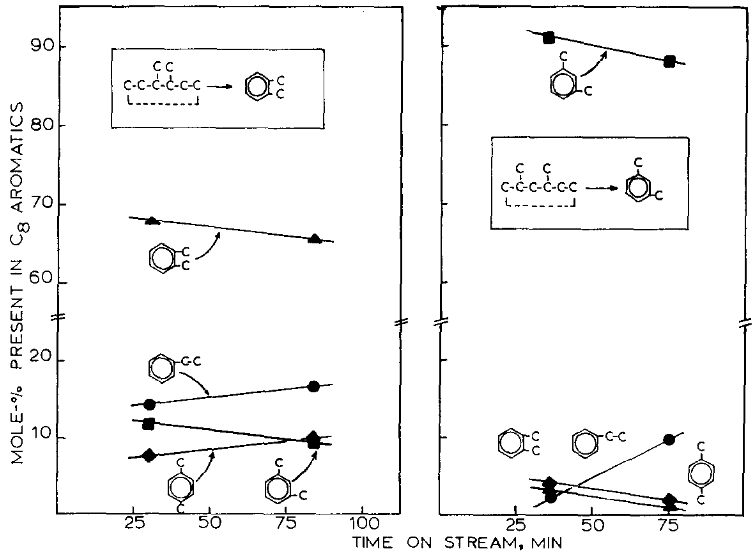


FIG. 4. Product distributions in the liquid $C_8$-aromatic fraction from the dehydrocyclization of 3,4- and 2,4-dimethylhexanes over Pt–$Al_2O_3$–K.

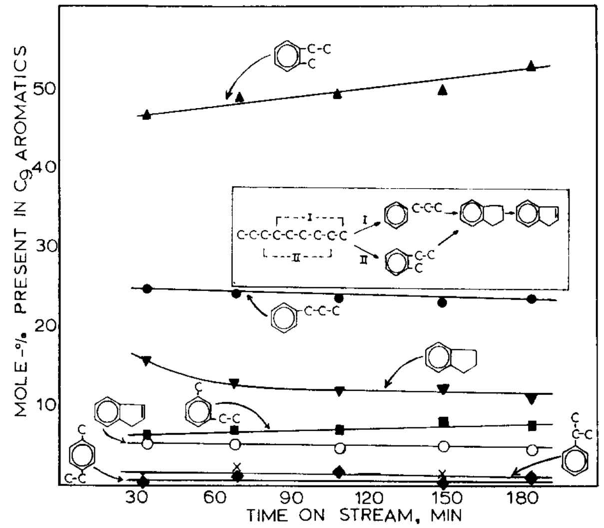


FIG. 5. Product distributions of the liquid $C_9$-aromatic fraction in the dehydrocyclization of *n*-nonane over Pt–$Al_2O_3$–K.

methylhexane is the one expected for direct 1,6-ring closure. However, the relative amounts of minor $C_8$-aromatics are not in agreement with the $C_8$-aromatic distribution expected for successive 1,2-methyl migrations. This problem is considered in more detail in the "Discussion" section.

Figure 5 presents results for the dehydrocyclization of *n*-nonane. The prediction of aromatic products is more complicated for this paraffin than for *n*-octane since the primary products may undergo a second cyclization to the indane system. As shown in Fig. 5, considerable indane and indene are formed. 2-Ethyltoluene and *n*-propylbenzene were passed over the catalysts under the same reaction conditions as used for *n*-nonane aromatization; the results are presented in Table 1. *n*-Propylbenzene and 2-ethyltoluene underwent about equal conversion to the indane system under our experimental conditions. If these two aromatics behave similarly during the run with *n*-nonane, the ratio of *n*-propylbenzene:2-ethyltoluene would be approximately 1:2. In any event, more than 90% of the $C_9$-aromatic products are the isomers expected for direct 1,6-ring closure.

Results for the aromatization of the three methyloctane isomers are presented in Figs. 6 and 7 and in Table 2. The major $C_9$-aromatic products for 3- and 4-methyloctane are in excellent agreement with those predicted by direct 1,6-ring closure.

TABLE 1

CONVERSION OF 2-ETHYLTOLUENE AND *n*-PROPYLBENZENE OVER Pt-$Al_2O_3$ AT 482°C

| | | Liquid product composition (mole %) | | | | | |
|---|---|---|---|---|---|---|---|
| Reactant | Sample | Benzene | Toluene | Indane | Indene | 2-Ethyltoluene | *n*-Propylbenzene |
| 2-Ethyltoluene[a] | 1 | 2.3 | 1.5 | 18 | 13 | 59 | <0.1 |
| | 2 | — | — | 16 | 12 | 67 | <0.1 |
| | 3 | — | — | 14 | 11 | 70 | <0.1 |
| *n*-Propylbenzene[a] | 1 | 1.0 | 3.9 | 20 | 12 | <0.1 | 54 |
| | 2 | 1.0 | 2.5 | 17 | 10 | <0.1 | 61 |
| | 3 | — | — | 15 | 8.6 | <0.1 | 65 |

[a] Other minor products were present in the liquid products.

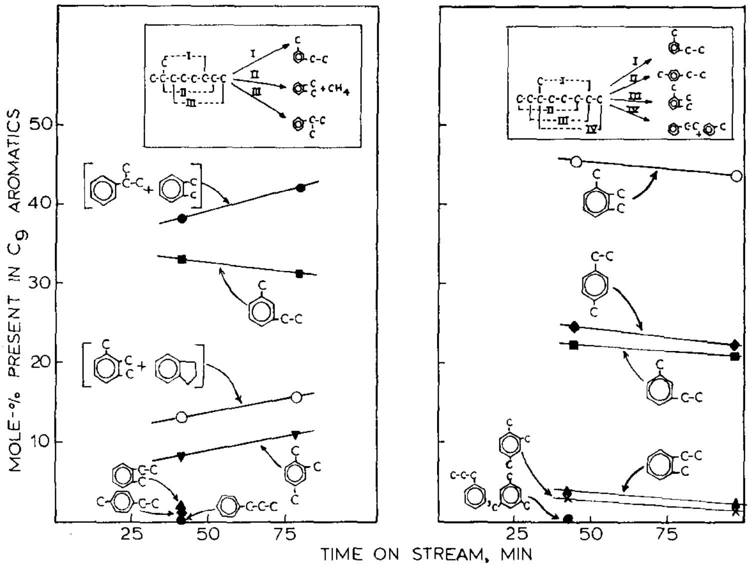


FIG. 6. Product distributions of the liquid $C_9$-aromatic fraction in the dehydrocyclization of 2- and 3-methyloctane over Pt–$Al_2O_3$–K.

The two $C_9$-aromatic products predicted by direct 1,6-ring closure for 2-methyloctane were present as the major products. However, considerable $C_9$-aromatic products—1,2,3- and 1,2,4-trimethylbenzene and indane—not predicted by 1,6-ring closure were present. The 1,2,3-trimethylbenzene could be the result of methyl migration from the 2- to the 3-position in the reactant paraffin. The only methyloctane

TABLE 2

AROMATIC PRODUCTS FOR DEHYDROCYCLIZATION OF METHYLOCTANES OVER Pt–$Al_2O_3$ AT 482°C[a]

| Aromatic product (mole %) | Reactant | | |
|---|---|---|---|
| | 2-Methyloctane | 3-Methyloctane | 4-Methyloctane |
| Isopropylbenzene | 35[b] | | |
| *n*-Propylbenzene | <1 | <1 | 9.9 |
| *p*-Ethyltoluene | <1 | 17 | <1 |
| *m*-Ethyltoluene | 31 | 16 | 20 |
| *o*-Ethyltoluene | 1.7 | 3 | 8.1 |
| 1,3,5-Trimethylbenzene | <1 | <1 | <1 |
| 1,2,4-Trimethylbenzene | 7.7 | 3 | 37 |
| 1,2,3-Trimethylbenzene and indane | 12[c] | 33[d] | 9.9[e] |
| Indene | ~2 | — | 4.9 |
| Ethylbenzene | ~3 | ~7 | 2.5 |
| *p*-Xylene | ~1 | ~7 | 1.0 |
| *m*-Xylene | ~3 | ~7 | 3.3 |
| *o*-Xylene | b | ~7 | 3.0 |
| Toluene | — | ~7 | — |

[a] Product distribution for Sample 1 (first 0.4 nl collected).

[b] Not completely separated, appeared to be ca. 1:5 *o*-xylene:isopropylbenzene.

[c] Appeared to be about equal amounts of each.

[d] Only small amount of indane, if any.

[e] Only very small amount of 1,2,3-trimethylbenzene.

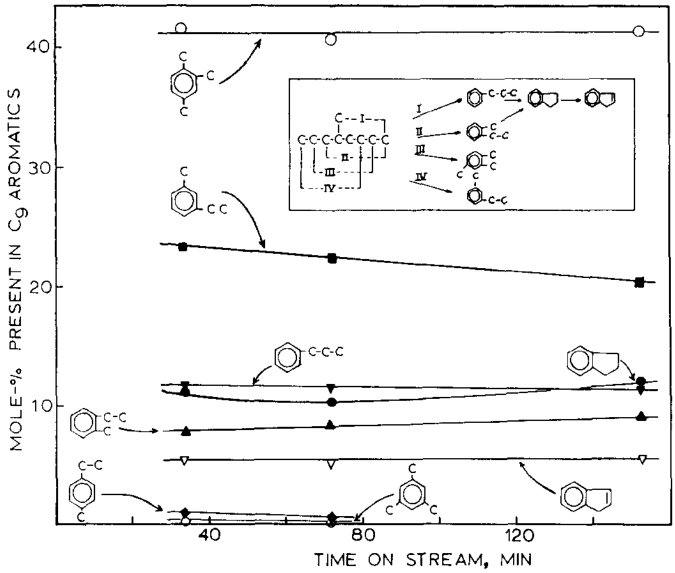


FIG. 7. Product distributions in the liquid $C_9$-aromatic fraction in the dehydrocyclization of 4-methyloctane over Pt–$Al_2O_3$–K.

which could form the indane and 1,2,4-trimethylbenzene by 1,6-ring closure is the 4-methyl isomer. The aromatic products obtained from 3-methyloctane show that isomerization to the 4-methyl isomer did not occur in a significant amount under the conditions of our experiment; thus we do not believe that methyl group migration is the only explanation for the unpredicted products obtained with 2-methyloctane.

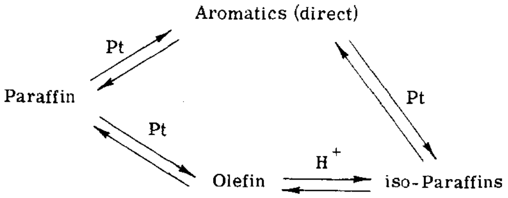
Small amounts of aromatics with fewer carbon atoms than the reactant paraffin were formed in all our studies. However, the amount of $C_8$-aromatics formed from 3-methyloctane is not small with respect to the $C_8$-aromatics formed from the other methyloctane isomers. Ethylbenzene is the only $C_8$ aromatic which should be formed from the geminal dialkyl intermediate, 1-ethyl-1-methylcyclohexane. The major $C_8$-product from 2-methyloctane, *o*-xylene, is explainable by a geminal dialkyl intermediate. However, about equal amounts of the four $C_8$-aromatics are formed from 3-methyloctane; furthermore, about 30% of the $C_8$–$C_9$ aromatics are $C_8$-aromatics. Toluene may also be formed from the geminal dialkyl intermediate for 3-methyloctane and is present in about the same amount as ethylbenzene.

## DISCUSSION AND CONCLUSIONS

As contrasted to mechanisms proposed more recently—where two or more ring size intermediates are involved—the mechanistic scheme for dehydrocyclization which featured direct six-member ring formation only allowed prediction of the isomeric aromatic products. As inferred earlier, many uncertainties still prevent definitive conclusions as to which of these mechanisms is really operative.

The major aromatic products obtained from the 10 different $C_8$–$C_9$ paraffin carbon skeleton structures used in our study are only those predicted by a direct six-membered ring closure. In all cases very small amounts of the isomers not expected for direct six-membered ring closure were obtained. Separate experiments with appropriate aromatics (in the presence of hydrogen) indicated that practically none of the aromatic would undergo conversion once it was formed; this conclusion is in agreement with results obtained by several workers using chromia catalysts (*1, 2*).

A probable source of the small amount of aromatic isomers, not allowed by direct six-member ring formation would be isomerization of the reactant by a small residual acidity, not neutralized by the alkali, prior to or during the cyclization step. The effect of an acidic alumina support was demonstrated using *n*-octane as reactant. In contrast to the nonacidic Pt–$Al_2O_3$, where more than 95% of the aromatic products were those predicted by direct six-member ring formation, the acidic Pt–$Al_2O_3$ catalyst produced more than 50% of the *m*- and *p*-xylene isomers. The acidic alumina did not cause appreciable xylene isomerization under our experimental conditions. Consequently, it appears that the aromatic isomers, not allowed by direct six-member ring formation, are formed from iso-paraffins which result from dual-functional catalytic reaction as shown:



The above type of reaction pathway has been advanced by other workers (*6, 16*).

Several of the paraffins used in this study, e.g., 2-methylheptane, could formally yield a geminal dialkylcyclohexane intermediate by one of the possible direct six-membered ring cyclization pathways. Our data suggest that such intermediates make an important contribution to the cyclization to aromatics.

The aromatic products obtained with 3,4-dimethylhexane are not in very good agreement with those predicted for direct six-membered ring formation. Furthermore, the distribution of the unpredicted aromatic isomers is not that expected for 1,2-methyl migration on the reactant prior to or during cyclization. Consecutive 1,2-methyl migrations would result in the isomer distribution *o*- $\gg$ *m*- $>$ *p*-xylene $>$ ethylbenzene. However, we obtained more ethylbenzene than *m*- or *p*-xylene. A possible explanation for this would be a Cope-type rearrangement of a 3,4-dimethylhexane diolefin structure to an *n*-octadiene followed by cyclization of the *n*-octadiene to form *o*-xylene and ethylbenzene.

Numerous attempts have been made to predict the amount of each aromatic isomer formed (*1–3, 17, 18*). The predictions have assumed a two-point adsorption of the paraffin and that all possible adsorptions which lead to six-member rings have equal probability for cyclization. For example, one would predict an ethylbenzene:*o*-xylene ratio of 2:1 since adsorption of the paraffin at the $C_1$–$C_2$ and $C_3$–$C_4$ atoms lead to ethylbenzene while *o*-xylene can result only from adsorption at the $C_2$–$C_3$ atoms. The above scheme for predicting the aromatic isomer distribution does not give a satisfactory accounting for the distribution we obtained experimentally. In fact, we find that different "nonacidic" catalyst supports may alter the aromatic isomer distribution without greatly increasing the amount of isomers not allowed by direct six-membered ring closure.

The relative reactivities of paraffin have been described in several publications (*2, 17, 18*). Accurate conversion data is difficult to obtain using our experimental conditions—conditions which are similar to those of much of the published data. Catalyst deactivation caused the conversion to decrease with time on stream; the deactivation rate may be very different for two reactants having similar initial reactivities. There is evidence to indicate that certain olefin isomers may cause more rapid deactivation even though the isomers show a similar initial reactivity (*19*). Consequently, the common practice of taking accumulative samples at increasing time on stream—the method also used in this study—will have the catalyst deactivation process superimposed on the reactivity of the paraffin. The order of reactivity based on gross samples which we obtained is in general agreement with those published by Herrington and Rideal (*17*). For example, our $C_8$-isomer reactivity was: *n*-octane $\cong$ 2,5-dimethylhexane $>$ 3-methylheptane $\cong$ 2-methylheptane $>$ 2,4-dimethylhexane $>$ 3,4-dimethylhexane.

These results and those of Fogelberg *et al.* (*8*) provide strong evidence for cyclization by direct six-member ring formation. They cannot eliminate the contribution of rings of other size, e.g., alkyl cyclopentanes, to side reactions such as coke formation or cracking to gaseous products. Furthermore, it must still be demonstrated that the results with Pt–$Al_2O_3$ can be extended to the chromia and chromia–alumina catalyst systems. Likewise, there is no strong evidence to show that these results obtained with a low hydrogen partial pressure are applicable at the higher hydrogen partial pressures encountered in a reforming process.

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