ACTA CHEMICA SCANDINAVICA 21 (1967) 2050–2060

Aromatization of Paraffin Hydrocarbons

II. Aromatization of C_8 Heptanes and Hexanes over Platinum/Alumina Catalysts

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The aromatization of C_8 heptanes and hexanes over two platinum/alumina catalysts, of quite different activity, in the temperature range 380—525°C is reported. Aromatics are formed mainly *via* 1,6 ring closure followed by a dehydrogenation step. The variety of aromatics formed at the higher temperatures with the more active catalyst would appear to result from isomerization before ring closure and not necessarily from any subsequent mechanistic change. In several examples the composition of the aromatic fraction obtained at 525° is compared with calculated values obtained from equilibrium data on C_8 paraffins. 2,2-Dimethylhexane and 3,3-dimethylhexane on direct 1,6 ring closure give a 1,1-dimethylcyclohexane structure whose dehydrogenation is blocked. Aromatic formation can be understood, however, if isomerization of these two paraffins to other isomers is recognized.

In the first paper of this series,[1] the aromatization of octane over platinum/alumina catalysts was discussed. The aromatization over the laboratory prepared platinum/α-alumina catalyst of low activity gave almost exclusively those compounds which could be formed by a direct closure to the six-membered ring. The mechanisms of Twigg [2] and Herington and Rideal [3] for aromatization over chromia/alumina could be applied to this system to explain these direct products. For the more active commercial platinum/alumina/halogen catalyst a greater variety of C_8 aromatics was obtained. To explain this, a major isomerization step was necessary and it was shown that this had to occur before formation of the six-membered ring. Under certain conditions, the octane was observed to isomerize to branched paraffins and it was proposed that these aromatized by six-ring formation to produce the final product distribution.

The present study is an extension of this work to cover the aromatization of a number of C_8 heptanes and hexanes, (namely 2-methylheptane, 3-methylheptane, 4-methylheptane, 3-ethylhexane, 2,3-dimethylhexane, 2,4-dimethylhexane, 2,5-dimethylhexane, 3,4-dimethylhexane, 2,2-dimethylhexane, and 3,3-dimethylhexane) over the two platinum/alumina catalysts mentioned.

The last two paraffins listed above are of particular interest as they both contain one fully substituted carbon atom. After ring closure the final step, dehydrogenation to the aromatic is blocked, and some isomerization or cracking reaction is needed to enable formation of aromatics.

EXPERIMENTAL

The reactor used for the aromatization reactions was similar to that of Kokes *et al.*[4] and has been described in detail previously.[1] Essentially the experimental procedure consisted of injecting small volumes (2—5 μl) of the hydrocarbons into a stream of hydrogen gas which passed over the catalyst in a micro-reactor. This was connected directly to a gas chromatograph (Perkin Elmer Model 154) thus enabling immediate and accurate analysis of the reaction products.

Meta- and *para*-xylene could not be separated with the column material used and the concentrations were determined using an infra-red technique discussed earlier.[1]

Materials. The C_8 heptanes and hexanes were obtained in high purity from the American Petroleum Institute.

Two platinum/alumina catalysts were used in this investigation. One was a high activity commercial platinum/alumina/halogen catalyst donated by Esso Ltd., and the other a laboratory prepared catalyst of low activity. The preparation of this latter catalyst has been described earlier [1] and contains the low activity α-alumina prepared from aluminium hydroxide by calcination at 1200°C. A low surface area of 40 m^2/g was measured for this catalyst.

Table 1. Aromatization of C_8 heptanes and hexanes over the laboratory prepared catalyst ($Pt/\alpha Al_2O_3$) at a temperature of 525°C and a hydrogen pressure of 1.5 atmospheres.

Hydrocarbon	Composition of C_8 aromatic fraction in mole %											
	Ethylbenzene			*o*-Xylene			*m*-Xylene			*p*-Xylene		
	Catalyst, g			Catalyst, g			Catalyst, g			Catalyst, g		
	0.4	1.0	1.45	0.4	1.0	1.45	0.4	1.0	1.45	0.4	1.0	1.45
2-Methylheptane	1.4	1.8	1.7	1.4	2.1	2.0	93.8	93.6	94.2	3.4	2.5	2.1
3-Methylheptane	17.5	17.1	16.5	25.0	25.0	24.8	2.0	1.9	2.1	55.5	56.1	56.6
4-Methylheptane	2.3	2.3	1.7	2.6	2.4	1.7	96.0	95.3	96.6	tarce	trace	trace
3-Ethylhexane	92.9	90.0	88.7	1.8	2.5	2.8	3.1	5.4	5.9	2.2	2.1	2.6
2,3-Dimethylhexane	0.9	0.7	0.9	91.8	91.7	90.5	5.4	5.3	6.0	1.9	2.2	2.6
2,4-Dimethylhexane	1.1	1.6	1.4	1.0	1.6	2.2	96.0	91.2	87.0	1.9	5.6	9.4
2,5-Dimethylhexane	trace	trace	0.1	trace	0.3	0.4	trace	2.2	3.2	~100	97.5	96.3
3,4-Dimethylhexane	3.0	4.0	4.1	89.9	87.0	86.2	5.4	5.3	5.8	1.7	3.7	3.9
2,2-Dimethylhexane	5.0	6.0	5.9	17.0	22.1	24.2	63.5	58.4	57.0	14.5	13.5	12.9
3,3-Dimethylhexane	9.3	9.0	9.1	27.7	27.9	27.9	48.2	48.0	48.2	14.8	15.1	14.8

RESULTS

The results of passing the various C_8 heptanes and hexanes over the laboratory prepared platinum/α-alumina catalyst at 525°C are shown in Table 1. With the exception of 2,2-dimethylhexane and 3,3-dimethylhexane, aromatization of these paraffins gave almost 90—100 % those aromatics which can be formed by a direct closure to a six-membered ring. Contact time, varied by using different amounts of catalyst in the reactor, had practically no effect on the composition of the C_8 aromatic fraction. The yields of aromatic compounds obtained with this catalyst increased with the amount of catalyst used, but varied for the different hydrocarbons. The highest yields were obtained with 2,5-dimethylhexane which gave a 33 % conversion over 1.45 g

Table 2. Aromatization of 2-methylheptane over the commercial catalyst (Pt/Al_2O_3/halogen) with hydrogen pressure of 1.5 atomspheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	9	—	5.4	10.0	24.8	40.7	19.1
525	0.3	47	4.8	12.7	7.8	20.8	35.9	18.0
525	1.0	52	6.4	17.5	5.9	19.0	33.9	17.3
380	1.0	6	—	1.0	2.9	15.5	64.5	16.1
400	1.0	14	—	2.0	6.2	20.4	49.5	21.7
425	1.0	21	—	2.9	8.5	23.0	43.3	22.4
450	1.0	45	0.4	4.4	9.3	24.2	41.0	20.7
475	1.0	49	1.9	6.7	9.2	24.2	38.8	19.2
500	1.0	51	4.4	11.5	7.1	22.8	36.3	17.9
525	1.0	52	6.4	17.5	5.9	19.0	33.9	17.3

Table 3. Aromatization of 3-methylheptane over the commercial catalyst (Pt/Al_2O_3/halogen) with a hydrogen pressure of 1.5 atmospheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	10	—	4.4	11.3	25.2	36.0	23.1
525	0.3	53	6.0	13.7	10.0	21.5	28.1	20.6
525	1.0	60	7.3	17.2	8.3	20.4	26.8	20.0
380	1.0	6	—	1.0	8.5	21.4	30.1	39.0
400	1.0	16	—	1.8	10.3	24.1	30.8	33.0
425	1.0	22	—	3.3	10.6	26.0	31.5	28.5
450	1.0	53	0.5	5.5	11.0	25.5	31.5	26.0
475	1.0	57	2.5	7.4	9.9	24.7	31.2	24.3
500	1.0	59	5.1	11.9	9.3	22.2	29.1	22.4
525	1.0	60	7.3	17.2	8.3	20.4	26.8	20.0

of catalyst at 525°C and decreased in the order octane > methylheptanes > ethylhexane > 3,4-, 2,4- and 2,3-dimethylhexanes > 2,2- and 3,3-dimethylhexane. With the last two compounds a conversion of approximately 1 % was obtained. In comparison with the commercial catalyst discussed below, the activity of this laboratory prepared catalyst, particularly its isomerizing and dehydrocyclizing power, was very low.

In Tables 2—11 the effects of temperature and contact time on the aromatization of the heptanes and hexanes over the commercial platinum/alumina/halogen catalyst are recorded. The yield of aromatics from all the paraffins used increased with temperature, chiefly in the range 415—450°, reached a maximum of approximately 60 % at about 500—525°C and decreased slightly

Table 4. Aromatization of 4-methylheptane over the commercial catalyst (Pt/Al_2O_3/halogen) with a hydrogen pressure of 1.5 atmospheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	10	—	5.3	13.3	23.1	39.8	19.6
525	0.3	54	9.1	13.1	9.3	20.2	33.0	15.3
525	1.0	59	10.7	20.7	7.5	16.3	31.0	13.7
380	1.0	6	—	1.8	14.0	22.1	52.8	9.3
400	1.0	15	—	2.1	14.1	24.2	44.8	14.8
425	1.0	21	—	3.3	13.7	25.9	41.5	15.9
450	1.0	50	0.7	5.5	12.5	25.1	40.0	16.2
475	1.0	54	3.4	6.9	10.9	24.8	37.8	16.2
500	1.0	59	6.8	11.6	9.7	21.9	35.0	15.0
525	1.0	59	10.7	20.7	7.5	16.3	31.0	13.7

Table 5. Aromatization of 3-ethylhexane over the commercial catalyst (Pt/Al_2O_3/halogen) with a hydrogen pressure of 1.5 atmospheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	10	—	4.7	18.0	21.9	35.6	19.8
525	0.3	52	9.5	14.3	14.3	18.0	26.2	17.7
525	1.0	60	11.0	17.2	11.0	18.1	25.2	17.5
380	1.0	7	—	1.3	21.2	16.8	35.2	25.5
400	1.0	15	—	1.9	21.4	20.2	33.3	23.2
425	1.0	24	—	2.8	19.0	22.7	33.1	22.4
450	1.0	52	0.8	5.0	16.0	23.6	32.8	21.8
475	1.0	54	3.9	6.3	12.5	23.4	32.5	21.4
500	1.0	59	6.5	11.2	12.0	21.2	30.6	18.5
525	1.0	60	11.0	17.2	11.0	18.1	25.2	17.5

Table 6. Aromatization of 2,3-dimethylhexane over the commercial catalyst (Pt/Al_2O_3/halogen) with a hydrogen pressure of 1.5 atmospheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	8	—	5.5	5.6	32.5	39.7	16.7
525	0.3	47	6.6	15.2	5.0	25.7	32.3	15.2
525	1.0	61	7.1	19.0	3.4	25.0	31.4	13.9
380	1.0	3	—	1.7	2.7	48.1	37.0	10.0
400	1.0	10	—	2.4	3.5	38.8	38.2	17.1
425	1.0	18	—	3.4	5.7	33.2	39.3	18.4
450	1.0	45	0.4	6.5	6.4	30.3	38.3	18.1
475	1.0	49	2.3	7.8	6.6	28.5	37.6	17.2
500	1.0	61	4.6	11.8	4.9	27.3	35.2	16.2
525	1.0	61	7.1	19.0	3.4	25.0	31.4	13.9

Table 7. Aromatization of 2,4-dimethylhexane over the commercial catalyst with a hydrogen pressure of 1.5 atmospheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	5	—	6.0	6.9	21.4	44.0	21.7
525	0.3	34	5.3	15.3	5.6	19.4	35.6	18.9
525	1.0	43	5.7	17.4	4.9	18.6	35.8	17.6
380	1.0	2	—	2.5	2.0	8.0	64.2	23.3
400	1.0	6	—	2.7	3.7	14.6	55.3	23.7
425	1.0	9	—	3.9	5.0	19.0	49.1	22.9
450	1.0	33	0.4	6.7	5.9	22.0	43.5	21.5
475	1.0	34	1.8	9.3	5.9	22.9	40.0	20.1
500	1.0	41	3.3	12.6	5.6	21.6	37.5	19.3
525	1.0	43	5.7	17.4	4.9	18.6	35.8	17.6

Table 8. Aromatization of 2,5-dimethylhexane over the commercial catalyst (Pt/Al_2O_3/halogen) at a hydrogen pressure of 1.5 atmospheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	8	—	4.1	3.9	15.0	31.7	45.3
525	0.3	49	3.2	16.5	2.8	11.6	26.8	37.1
525	1.0	59	3.6	18.3	1.9	11.3	26.5	36.5
380	1.0	6	—	0.5	0.3	1.8	5.9	91.5
400	1.0	14	—	0.8	0.6	2.8	12.5	83.3
425	1.0	21	—	1.5	2.4	7.1	19.0	70.1
450	1.0	41	0.2	4.0	2.8	11.3	22.1	59.5
475	1.0	43	1.0	7.4	3.0	13.0	26.4	50.0
500	1.0	57	2.2	11.6	2.9	12.3	28.4	42.6
525	1.0	59	3.6	18.3	1.9	11.3	26.5	36.5

Table 9. Aromatization of 3,4-dimethylhexane over the commercial catalyst (Pt/Al_2O_3/halogen) at a hydrogen pressure of 1.5 atmospheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	8	—	6.1	8.6	27.0	39.1	19.2
525	0.3	46	7.7	15.8	6.7	22.4	31.0	16.4
525	1.0	58	9.5	22.0	2.9	21.4	29.2	15.0
380	1.0	4	—	2.0	7.6	42.8	30.0	17.6
400	1.0	11	—	2.1	7.7	35.9	34.2	19.2
425	1.0	18	—	3.3	8.3	32.0	36.4	20.1
450	1.0	46	0.5	6.0	8.5	29.0	36.4	19.6
475	1.0	52	3.2	7.8	7.5	27.1	35.0	18.4
500	1.0	57	6.5	12.2	6.4	24.8	33.0	17.1
525	1.0	58	9.5	22.0	2.9	21.4	29.2	15.0

Table 10. Aromatization of 2,2-dimethylhexane over the commercial catalyst at a hydrogen pressure of 1.5 atmospheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	5	—	10.0	7.8	20.2	42.1	19.8
525	0.3	47	4.5	18.0	5.2	23.4	31.9	15.0
525	1.0	59	6.8	22.4	3.0	23.2	24.7	19.9
380	1.0	1	—	4.9	2.8	25.4	49.0	17.9
400	1.0	4	—	5.0	3.5	29.0	39.0	23.5
425	1.0	11	—	5.9	4.9	30.0	33.7	25.5
450	1.0	33	0.4	7.7	6.0	29.6	31.2	25.1
475	1.0	49	1.8	9.6	6.0	28.6	28.8	24.8
500	1.0	60	4.2	14.9	4.7	26.3	26.2	23.6
525	1.0	59	6.8	22.4	3.0	23.2	24.7	19.9

thereafter. The composition of the aromatic fraction varied appreciably with temperature; however, those aromatics whose formation required only a direct ring closure and dehydrogenation again appeared in the largest concentration even at the highest temperatures. An exception to this was 3-ethylhexane which gave *m*-xylene as the major product throughout the temperature range. The relative amounts of toluene and benzene in the aromatic fraction from all the paraffins increased with increasing reaction temperature, toluene appearing in the reaction products at 380°C but benzene only when the temperature had reached 450°C. The longer contact times increased the amount of aromatic products but maintained approximately the same proportions for the different C_8 aromatics. The amounts of toluene and benzene from cracking reactions increased with contact time as expected.

Table 11. Aromatization of 3,3-dimethylbenzene over commercial catalyst with a hydrogen pressure of 1.5 atmospheres.

Temp. °C	Wt. of catalyst (g)	Conversion to aromatics	Composition of aromatic fraction in mole %					
			Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
525	0.1	7	—	7.4	8.4	27.3	40.5	16.4
525	0.3	47	6.0	17.3	6.2	23.2	32.0	15.2
525	1.0	58	6.8	20.5	4.5	23.0	31.2	14.0
380	1.0	3	—	2.1	4.7	44.9	36.2	12.1
400	1.0	9	—	2.7	5.5	37.8	37.8	16.2
425	1.0	16	—	3.7	5.7	33.0	37.6	18.3
450	1.0	40	0.3	6.2	7.1	29.8	37.4	19.3
475	1.0	53	2.7	9.0	7.0	27.2	35.4	18.7
500	1.0	58	5.3	13.0	6.0	24.9	33.6	17.1
525	1.0	58	6.8	20.5	4.5	23.0	31.2	14.0

DISCUSSION

Aromatization over the laboratory prepared platinum/α-alumina catalyst. With the exception of 2,2-dimethylhexane and 3,3-dimethylhexane which will be discussed later, the aromatization of these hydrocarbons over the laboratory prepared platinum/α-alumina catalyst is best explained by the mechanisms of Twigg[2] and Herington and Rideal,[3] applied in the same manner as to octane reactions over this catalyst.[1] This involves closure of an adsorbed olefinic species to a six-membered ring, followed by a dehydrogenation step.

The case of 2-methylheptane is slightly complicated since one of the possible ring closures shown in Fig. 1 gives rise to a ring whose subsequent dehydrogenation is blocked by the disubstituted carbon atom.

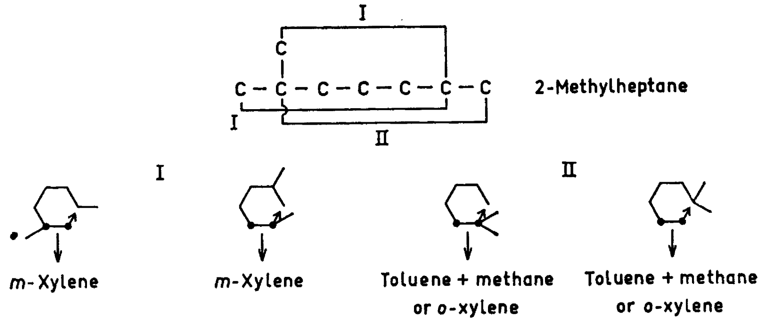

Fig. 1. Possible closures to six-membered rings and products from 2-methylheptane (the dots represent adsorbed carbon atoms on the catalyst surface).

Dehydrogenation can occur, however, by first splitting off a methyl group[5] or by rearrangement of the 1,1-dimethylhexane structure to produce mainly *o*-xylene.[6] In practice only about 2 % *o*-xylene was produced over this catalyst at 525°C indicating that the other ring closures giving *m*-xylene are much more favourable. This result is in accordance with the low acidic character and isomerizing ability of the catalyst.

Aromatization of 3-methylheptane over the platinum/α-alumina catalyst at 525°C gave 17 % ethyl-benzene, 25 % *o*-xylene, 2 % *m*-xylene and 56 % *p*-xylene, figures which are very similar to those of Herington and Rideal[3] who used a chromia/alumina catalyst. If all the ring closures for this hydrocarbon (Fig. 2) are possible, then ethylbenzene, *o*-xylene, and *p*-xylene should be formed in equal amounts. However, structures Ib and IIb are sterically unfavourable and a recalculation will give values[3] of 20 % ethylbenzene, 20 % *o*-xylene and 60 % *p*-xylene. The additional discrepancy with the experimental results may arise from the fact that *o*-xylene formation involves ring closure between secondary and primary carbon atoms as opposed to two primary carbon atoms for ethylbenzene formation.[5]

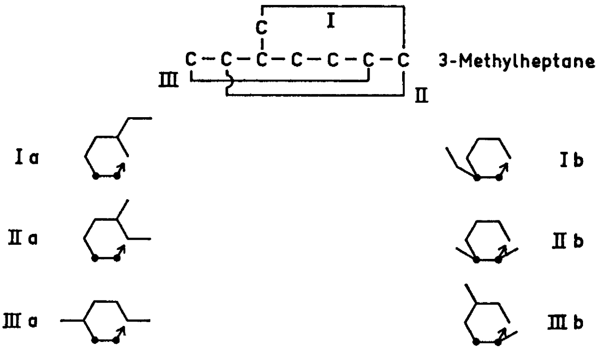

Fig. 2. Possible closures to six-membered rings with 3-methylheptane (the dots represent carbon atoms adsorbed on the catalyst surface).

With 4-methylheptane, 3-ethylhexane, 2,3-dimethylhexane, 3,4-dimethylhexane, 2,4-dimethylhexane, and 2,5-dimethylhexane aromatization *via* closure to the six-membered ring intermediate provides an explanation of 90—100 % of the aromatics produced.

Aromatization over the commercial platinum/alumina/halogen catalyst. Aromatization of these paraffin hydrocarbons over the active commercial platinum/alumina/halogen catalyst is more complicated. However, with the exception of 3-ethylhexane, the results of the aromatization at 380°C agree with those obtained over the platinum/α-alumina catalyst in that the major products are the same. Since the other products cannot be accounted for by a direct six ring closure and dehydrogenation of the injected hydrocarbon, other explanations are required. It has been shown previously[1] that with this catalyst isomerization after closure to a six-membered ring is negligible.

Passage of individual C_8 aromatics over the commercial catalyst gave less than 4 % of the other C_8 isomers while the corresponding alkylcyclohexanes gave only slightly greater isomerization.[1] In the same paper,[1] the diverse C_8 aromatic composition obtained when octane was passed over this catalyst at the higher temperature was explained by isomerization of the injected octane to methylheptanes and dimethylhexanes which then aromatized *via* closure to six-membered ring intermediates. Paraffin hydrocarbons have been shown[8–10] to undergo such isomerizations over similar platinum/alumina catalysts and in the study reported here evidence of the presence of other isomeric paraffins in the reaction mixture was also observed in gas chromatograms when low temperatures or short contact time were used. The isomerizing ability of these reactive catalysts is usually considerably greater than the dehydro-cyclizing power and since both reactions increase with temperature[11] it may be anticipated that the resulting aromatic composition is related to the extent to which isomeric paraffins are formed before ring closure. Using the data of Rossini *et al.*[12] for equilibria of paraffins, and assuming that only normal, methyl substituted, and dimethyl substituted paraffins are produced fast enough to be considered in the subsequent reactions, the composition of the resulting aromatic fraction can be estimated. Table 12 shows the calculated composition of the C_8 aromatic fraction at 525°C from equilibrium data, assuming closure to a six-membered ring, together with the experimental composition of the aromatic fraction obtained with the aromatization of 2-methylheptane, 3-methylheptane, 4-methylheptane, and 3-ethylhexane. Considering the complexity of the reactions occurring and the approximate nature of the calculations, the values show fairly good agreement.

Table 12. Comparison of experimental and theoretical values for the composition of the C_8 aromatic fractions.

		Mole %			
		Ethylbenzene	*o*-Xylene	*p*-Xylene	*m*-Xylene
Calculated composition at 525°C		18.7	21.9	19.8	39.6
Experimental	2-methylheptane	7.8	25.0	22.7	44.5
»	3-methylheptane	11.0	27.0	26.5	35.5
»	4-methylheptane	11.0	23.8	20.0	45.3
»	3-ethylhexane	15.3	25.2	24.4	35.1

Pines *et al.*[13–15] have postulated that aromatization can occur *via* five-, six-, seven-, and eight-membered ring intermediates but this was for chromia/alumina catalysts of low acidic character. Low acidity was said to favour the larger rings, so that if such mechanisms apply to an active platinum/alumina catalyst formation of five-membered rings is most probable. Kasanski and Liberman[16] have also explained the aromatization of substituted pentanes *via* a five-membered ring which presumably then expands to the six-membered ring *via* a carbonium ion mechanism.[6] However, such a scheme involving five-membered ring intermediates will not explain all C_8 aromatic formation, for instance *p*-xylene and ethylbenzene from 2,3-dimethylhexane. In this case at least, aromatization *via* formation of five-membered ring intermediates is not a major mechanism. It is conceivable that isomerization does occur after formation of the five-membered ring but should not involve multiple ring expansion and contraction [17,18] for the reasons already stated.

Aromatization of 2,2-dimethylhexane and 3,3-dimethylhexane. 2,2-Dimethylhexane and 3,3-dimethylhexane give similar results when passed over either the laboratory or the commercial catalyst, a variety of C_8 aromatics being formed. Both these paraffins can close to a six-membered ring, but give a 1,1-dimethylcyclohexane structure so that dehydrogenation to aromatics is blocked. It has been reported [5] that compounds having this cyclic structure containing geminal dimethyl groups give mainly toluene and methane when passed over chromia/alumina catalysts of low activity, presumably by splitting off one of the methyl groups. Keulmans and Voge [6] passed 1,1-dimethylhexane over a platinum/alumina/halogen catalyst at 350°C and obtained *o*-xylene and traces of toluene as the only aromatic products. The aromatic distribution obtained in the present studies must therefore require isomerization steps, probably before ring closure. For the commercial catalyst isomerization of the paraffins *via* known carbonium ion mechanisms, already mentioned in connection with octane,[1] can occur.

Rearrangements over the platinum/α-alumina catalyst of low activity is also possible to a certain extent by an ionic mechanism. In addition Pines *et al.*[15] have used a non-ionic mechanism to explain skeletal rearrangements over chromia/alumina of low acidic character. The mechanism [15,20] involves a methyl carbon insertion *via* a vinyl migration, which gives a 2-methylheptane structure from 2,2-dimethylhexane and a 3- or 4-methylheptane structure from 3,3-dimethylhexane. Other isomeric paraffins can be formed from the original paraffin *via* a similar mechanism involving cyclobutane adsorbed species.[15,19]

In conclusion, it would seem that the aromatization of a specific paraffin may be represented schematically as shown in Fig. 3.

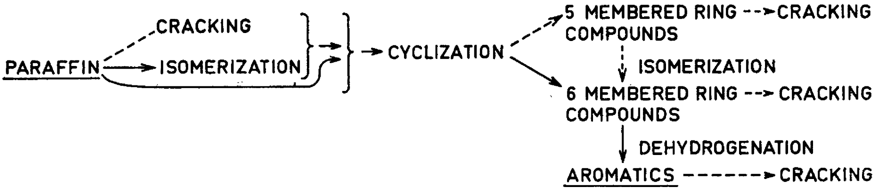

Fig. 3. Schematic representation of aromatization of C_8 paraffins.

Aromatization *via* six-membered ring intermediates seems to predominate and isomerization of the initial paraffin becomes appreciable when using the active commercial catalyst at the higher temperatures.

Acknowledgements. Financial support from the *Swedish Council for Applied Research (Statens Tekniska Forskningsråd)* is gratefully acknowledged.

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Received April 29, 1967.