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Aromatization of Paraffin Hydrocarbons

I. Aromatization of Octane

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The aromatization of octane is investigated in the temperature range 380—525°C chiefly over two platinum/alumina catalysts. Preliminary results are also given for various chromia/alumina catalyst compositions. A micro-reactor is used, coupled directly to a gas-chromatograph for easy analysis of the aromatics formed. Closure of the paraffin predominantly to six-membered ring intermediates is believed to occur, followed by dehydrogenation to aromatics. The diverse composition of the aromatic fraction obtained at the higher temperatures, particularly with the more active catalyst, is attributed to isomerization steps before ring closure. Evidence is given to substantiate these conclusions and the results are discussed in the light of earlier investigations.

Since the early work of Moldavsky and Kamuscher[1] using chromium and molybdenum oxides and of Kazanski and Plate[2] using platinum catalysts to bring about the reforming of hydrocarbons, considerable effort has been expended on this problem stimulated mainly by the requirements of the petroleum industry to produce high octane fuels.

However, despite the success of the industrial processes, the mechanisms by which the chemical conversions take place over the various catalyst systems remain obscure. Numerous studies of the principle reactions occurring in the reforming process (namely dehydrocyclization, dehydrogenation, isomerization, cracking to lower molecular weight products, and the detrimental deposition of carbonaceous material on the catalyst) have indicated the most efficient catalysts and conditions to be used in upgrading low octane charges consisting of paraffinic and cycloparaffinic compounds to high octane aromatic and isoparaffinic products.

It is generally accepted that a potential reforming catalyst is required to perform two functions these being (a) isomerization brought about by acidic sites and (b) hydrogenation-dehydrogenation, which in the case of metal/metal oxide catalysts clearly derives from metal sites.

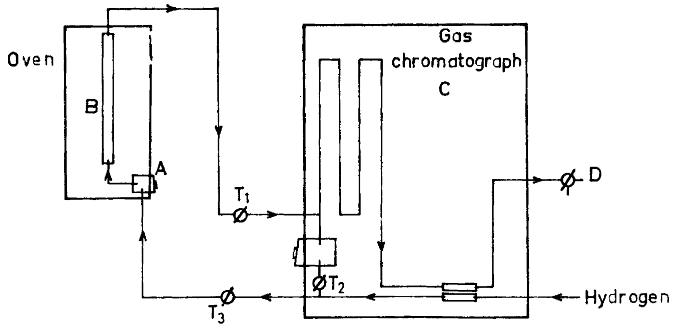

Fig. 1. Apparatus used for studying reformation reactions of hydrocarbons.

Chromia/alumina catalysts have been most extensively studied and recently Pines and coworkers[3] have contributed much to the understanding of the mechanisms that can occur over this type of catalyst. Bifunctional catalysts such as platinum/alumina, because of the milder operating conditions that they allow, are extensively used in industrial processes and have been the subject of a number of reviews.[4-6]

EXPERIMENTAL

The apparatus used for the aromatization reactions is illustrated schematically in Fig. 1 and was of a similar construction to that used by Kokes *et al.*[7] Small volumes (2—5 μl) of hydrocarbon were injected into a hydrogen gas stream (60 ml/min) at A and passed over the catalyst in a microreactor B connected directly to a chromatograph C. Fractions could be collected at D after emerging from the chromatograph and analysed by other techniques. By switching the taps T_1, T_2, and T_3 the hydrocarbon could be injected immediately onto the chromatograph column. The micro-reactor consisted of a stainless steel tube 33 cm long with an internal diameter of 7 mm placed in the centre of a vertically mounted, electrically heated oven. The catalyst was held in position in the tube by glass wool plugs. A heated injection block was situated immediately up-stream of the reactor. The reactor itself was connected to the gas-chromatograph *via* a stainless steel capillary tube (1 mm internal diameter) which was heated and heavily insulated with asbestos tape to prevent condensation of the reaction products. High grade hydrogen was further treated for removal of final traces of oxygen before use by passage over a palladium catalyst in an Engelhard catalytic Deoxo-purifier.

The gas chromatograph used was a Perkin-Elmer model 154. A stationary phase composed of 20 % *p*-nitroaniline picrate and 2 % squalane on Chromosorb[8] (60—80 mesh) gave a good separation of aromatics from paraffins, olefins, and naphthenes.

It was not possible to separate the *m*- and *p*-xylene isomers with the stationary phase used. Instead the reaction products were taken up in cyclohexane and the solution analysed with a Beckman Model I.R.9 infrared spectrophotometer. *m*- and *p*-Xylenes have absorption peaks at 770 and 795 cm^{-1}, respectively,[9] and the intensity of these absorptions were used to determine the ratio of the isomers present.

Materials

Octane of "Puriss" quality was obtained from Fluka AG;
ethylcyclohexane of "Puriss" quality was obtained from Kebo AB, Stockholm;
benzene, toluene, ethylbenzene, *m*-, *o*-, and *p*-xylene of "puriss" quality were obtained from Kebo AB.

The aromatizations were carried out over a variety of catalysts. A *commercial platinum/alumina/halogen catalyst* was donated by Esso Ltd. and other catalysts were prepared in the laboratory as described below.

Catalyst 1 was a chromia/alumina type where the alumina had been prepared from potassium aluminate.[10] Alumina (10 g) was calcined for 5 h at 610°C in a stream of nitrogen and after cooling was mixed into a solution of chromic acid (2.1 g) in distilled water (8.8 ml). The mixture was left to stand for one hour and then dried at 120°. It was finally calcined at 510°C for 3 h in a stream of dry air.

Catalyst 2 differed from catalyst 1 only in that it contained traces of potassium and cerium oxides.[11] Catalyst 1 (6.6 g) which had not been calcined at 510°C was added to a solution of potassium nitrate (0.15 g) and cerium nitrate (0.12 g) in distilled water (5 ml). The mixture was left in a covered glass for one hour and then dried at 120°C. The dry catalyst was finally calcined at 510°C for 3 h in a dry stream of air.

Catalyst 3 was another chromia/alumina type, where the alumina had this time been prepared by hydrolysis of aluminium isopropoxide.[11,12] A dry sample of this alumina was calcined at 620°C for 4 h in a dry nitrogen stream and after crushing and sieving, particles between 28 and 65 mesh were treated with chromic acid as for catalyst 1.

Catalyst 4 was a sample of catalyst 3 with traces of potassium and cerium oxides introduced as with catalyst 2.

Catalyst 5 was a platinum/alumina type where the alumina was obtained from aluminium hydroxide by calcination at 1200°C. This α-aluminium oxide was obtained from Höganäs-Billesholm AB. A sample (3 g of 28—65 mesh) was made completely wet by addition of 2 ml of a 5×10^{-2} M solution of hexachloroplatinic acid in water and left in a covered vessel for one hour. It was then dried at 100°C for 18 h and finally calcined at 610°C for 3 h in a slow stream of dry air.

The surface areas of the catalysts were determined by the continuous flow method of Nelson and Eggertsen [13] using a Perkin-Elmer-Shell Model 212 B Sorptometer.

The activity of freshly prepared catalysts was irregular and each sample was stabilized in the following way before use. A slow stream of hydrogen gas was passed through the catalyst bed and the temperature of the oven gradually raised to 400°C over a period of 3 h. This temperature was maintained for a further 4 h and then raised to 500°C. The stabilization was completed by a series of injections of octane at this temperature until a constant activity was observed for three consecutive injections. Usually about ten injections were required. Subsequently, the activity was checked from time to time by aromatizing octane and ethylcyclohexane under standard conditions.

RESULTS AND DISCUSSION

The results obtained when octane was passed over the commercial platinum/alumina/halogen catalyst are shown in Table 1. The conversion to aro-

Table 1. Aromatization of octane using 1.0 g of commercial catalyst and a hydrogen pressure of 1.5 atmospheres.

	Conversion	Composition of aromatic fraction in mole %					
Temp.	to aromatics	Benzene	Toluene	Ethyl-benzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
380	10	—	0.8	28.9	49.8	8.4	2.1
400	19	—	1.0	30.5	42.2	19.7	6.5
425	25	—	1.2	27.5	35.1	25.1	11.1
450	54	0.8	3.9	24.0	29.5	27.0	13.9
475	61	2.9	6.3	21.3	27.3	27.0	15.2
500	63	5.9	11.6	15.6	27.4	25.3	14.2
525	62	8.8	15.9	12.0	26.3	24.1	13.0

matics is seen to rise with temperature to a constant value of about 60 % at 500°C. The compounds which can be formed by a direct closure to a six-membered ring intermediate predominate at the lower temperatures but decrease in preference to other isomers at the higher temperatures indicating an increasing degree of isomerization. Large amounts of toluene and benzene are formed at the higher temperatures showing that appreciable decomposition *via* cracking can occur. In certain experiments involving low temperatures or short contact time the presence of other paraffins formed by isomerization of octane were observed in the gas chromatogram.

The effects of passing various C_8 aromatics and also the corresponding saturated cyclic compounds over the commercial catalyst at 525°C are shown in Tables 2 and 3, respectively. Very little isomerization occurs but again decomposition to benzene and toluene is obtained. The decomposition and the small amount of isomerization is slightly greater for the saturated compounds. Furthermore, the ethyl substituted compounds such as ethylbenzene and ethylcyclohexane show a greater tendency to decomposition than other isomers. This can be related to the relative strengths of the bonds involved, since the dissociation energy of CH_3-X is considerably larger

Table 2. Passage of C_8 aromatics over commercial catalyst. 1.0 g of commercial catalyst at a temperature of 525°C and a hydrogen pressure of 1.5 atmospheres.

	Composition of aromatic fraction in mole %					
Hydrocarbon	Benzene	Toluene	Ethyl-benzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
Ethylbenzene	16.7	26.4	56.5	0.3	0.1	trace
o-Xylene	0.4	16.1	0.1	79.3	2.8	1.3
m-Xylene	0.6	17.1	trace	2.0	79.3	1.0
p-Xylene	0.5	17.2	trace	0.6	2.6	79.1

Table 3. Aromatization of C_8-naphthenes over 1.0 g of commercial catalyst at 525°C and a hydrogen pressure of 1.5 atmospheres.

	Composition of aromatic fraction in mole %					
Hydrocarbon	Benzene	Toluene	Ethyl-benzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
Ethylcyclohexane	20.2	31.0	48.0	0.3	0.4	0.1
1-*cis*-2-Dimethyl-cyclohexane	0.9	15.8	0.2	77.9	3.2	2.0
1-*trans*-2-Dimethyl-cyclohexane	0.8	15.8	0.1	78.2	3.1	2.0
1,3-Dimethylcyclo-hexane	0.5	17.0	trace	2.3	78.4	1.8
1,4-Dimethylcyclo-hexane	0.9	21.8	0.1	1.0	1.6	74.6

when X is a phenyl group[14] than when it is a benzyl group.[15] The observation also provides a partial explanation of the decreasing amount of ethylbenzene in the aromatic fraction obtained by passing octane over the commercial catalyst at increasing temperatures.

Variation of contact time was obtained by using different amounts of catalyst in the reactor and the results obtained with octane over the commercial catalyst at 525°C are shown in Table 4. Both the degree of aromatization and the decomposition by cracking increase with contact time as expected. The large decrease in the concentration of ethylbenzene could again be partly accounted for by its higher cracking tendency.

Table 4. Aromatization of octane using varying quantities of commercial catalyst at a temperature of 525°C and a hydrogen pressure of 1.5 atmospheres.

Grams of catalyst	Conversion to aromatics in wt %	Composition of aromatic fraction in mole %					
		Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
0.1	13	—	3.5	22.8	30.0	27.5	16.1
0.3	50	6.9	11.7	18.7	28.4	20.8	13.4
1.0	62	8.8	15.9	12.0	26.3	24.1	13.0

Table 5. Aromatization of ethylcyclohexane using 1.0 g of commercial catalyst and a hydrogen pressure of 1.5 atmospheres.

Temp.	Conversion to aromatics	Ethylcyclohexane remaining %	Composition of aromatic fraction in mole %		
			Benzene	Toluene	Ethylbenzene
250	11	89	—	—	100
275	39	61	—	—	100
300	74	26	—	—	100
325	87	13	—	—	100
350	97	3	—	0.3	99.7
375	100	—	—	0.7	99.3
400	100	—	0.2	1.2	98.6
425	100	—	1.2	2.2	96.6
450	100	—	3.1	4.5	92.4

Table 5 shows the effect of temperature on the aromatization of ethylcyclohexane over the commercial catalyst. The conversion is complete at 375° giving almost exclusively ethylbenzene with small amounts of toluene and benzene by decomposition. At higher temperatures trace amounts of other C_8 isomers begin to appear.

Preliminary results of the aromatization of octane over various other catalysts at 525° are given in Table 6. In all cases the yield of aromatics is

Table 6. Aromatization of octane over various laboratory prepared catalysts. Temperature 525°C, a hydrogen pressure of 1.5 atmospheres and 1 g of catalyst.

Catalyst 1. Chromia on alumina prepared from potassium aluminate, specific area 200 m^2/g.

Catalyst 2. Catalyst 1 with small amounts of potassium and cerium oxides. Specific area 280 m^2/g.

Catalyst 3. Chromia on alumina, which had been prepared *via* hydrolysis of aluminium isopropoxide. Specific area 170 m^2/g.

Catalyst 4. Catalyst 3 with small amounts of potassium and cerium oxides. Specific area 210 m^2/g.

Catalyst 5. Platinum on α-alumina prepared by heating aluminium hydroxide to 1200°C. Specific area 40 m^2/g.

Catalyst	Composition of C_8-aromatic fraction in mole %			
	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
1	28.8	47.0	13.4	10.8
2	22.7	43.9	18.8	14.6
3	22.4	43.3	23.3	11.0
4	35.4	52.0	8.3	4.4
5	39.7	55.9	2.5	1.9

lower than with the commercial catalyst. The aromatization over platinum/α-alumina (catalyst 5) gives almost entirely those compounds, ethylbenzene and *o*-xylene which can be formed by direct closure to the six-membered ring indicating that the isomerizing ability of this catalyst is low. The effect of contact time on the composition of the aromatic fraction obtained by passing octane over this catalyst is shown in Table 7.

Table 7. Aromatization of octane over platinum/α-alumina at a temperature of 525°C and a hydrogen pressure of 1.5 atmospheres.

Weight of	Composition of C_8-aromatic fraction in mole %			
catalyst used (grams)	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
0.4	39.3	58.4	1.4	0.5
1.0	39.7	58.3	1.4	0.6
1.45	38.8	58.8	1.7	0.7

In devising a mechanism for the aromatization over the platinum/alumina catalysts it should be noted that no isomerization occurs after closure to a six-membered ring. Table 2 shows that passage of C_8 aromatics over the commercial catalyst gives less than 4 % of other C_8 isomers, while the alkylcyclohexanes (Table 3) give only slightly greater isomerization, these two facts being in agreement with the work of Pitts *et al.*[16] Thus, isomerization of partly or fully hydrogenated aromatics cannot account for the composition obtained by the aromatization of octane. In the same way it is clear that recombination of cracking products can only contribute to the isomerization in a small way.

For the octane-platinum/α-alumina system the aromatic formation is best explained by closure to a six-membered ring followed by dehydrogenation. According to the proposals of Twigg[17] and of Herington and Rideal[18] ring closure over a chromia/alumina catalyst involves an adsorbed olefin and can only occur between a carbon atom in the gas phase and one of the two atoms attached to the catalyst surface. Applying this idea to a platinum/alumina catalyst the following six-ring closures are possible for octane.

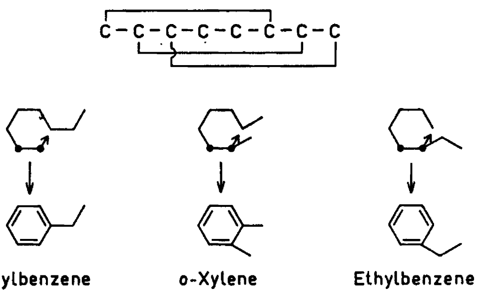

Fig. 2. Possible closures to six-membered ring with octane (the points represent carbon atoms which are adsorbed on the catalyst surface).

Using platinum/α-alumina catalyst No. 5 with octane 39 % ethylbenzene, 59 % *o*-xylene, and small amounts of *m*- and *p*-xylene are formed (Table 6). The fact that *o*-xylene is produced in greater amounts than ethylbenzene, although there is seemingly a greater probability for formation of ethylbenzene, may arise form a steric factor[18] and/or from the fact that *o*-xylene formation involves two secondary carbon atoms whereas closure to ethylbenzene is between one secondary and one primary carbon atom.[19]

The aromatization of octane over the commercial catalyst at low temperatures closely resembles that over platinum/α-alumina and it is reasonable to assume that a similar mechanism occurs under these conditions. In order to explain the aromatic composition at higher temperatures it is necessary to consider the properties of such catalysts, bearing in mind that isomerization under these conditions occurs before ring closure. Commercial catalysts in general have a high acidic character having been prepared from the more active gamma or eta forms of alumina[20] and further activated by addition of halogen. This enhanced acidic character will increase both the isomerization and cracking ability. There are many reports[5,6,21,22] of the isomerization of paraffins over these catalysts and in the present studies evidence of isomerization was observed at low temperatures or short contact times. In addition, isomerization is considerably faster than dehydrocyclization for such catalysts, both reaction rates increasing with temperature.[23] Thus, appreciable isomerization of the octane to methylheptanes and dimethylhexanes *etc.*, would be expected. These isomeric paraffins would undergo aromatization *via* closure to a six-membered ring as described above, thereby accounting for the obtained aromatic composition.

A rough check of this scheme can be made using the calculated values of the equilibrium concentrations of respective paraffins given by Rossini *et al.*[24] The various isomeric paraffins are assumed to undergo aromatization *via* six ring intermediates, when the composition of the resulting aromatic products can be estimated. However, the normal, monomethyl and, to a lesser extent, dimethyl substituted paraffins will have higher "effective" concentrations in the reaction mixture since they are produced faster than more highly branched paraffins. At 525°C the calculated values (19.8 % *p*-xylene, 39.6 % *m*-xylene, 21.9 % *o*-xylene, and 18.7 % ethylbenzene) for the composition of the resulting C_8 aromatic fraction are not unreasonable considering the approximate nature of the calculations and the numerous reactions that may occur.

Aromatization of paraffins *via* five-, six-, seven-, and eight-membered ring intermediates has been postulated by Pines *et al.*[3,25,26] using a non-acidic chromia/alumina catalyst. The lower acidity is said to favour the formation of the higher rings. Applying this principle to an active platinum/alumina catalyst closure to a five membered ring is most likely, followed by expansion to a six membered ring by a carbonium ion mechanism such as that discussed by Keulemans.[27] Although other mechanisms such as these may occur, their contribution to the final aromatic composition would seem to be quite small in our case.

The complex nature of aromatization over chromia/alumina catalysts does not allow any definite conclusions to be reached from the results given for octane in Table 6. However, several interesting points are worth discussing. It is well known that alumina not only acts as a support material but also has a definite acidic character whose strength depends on the method of preparation.[28] Alumina prepared from potassium aluminate has weak acidic sites whereas a sample prepared from aluminium isopropoxide has relatively strong acidic sites. This is clearly shown in Table 6; the chromia/alumina catalyst 3 gives much larger amounts of *m*- and *p*-xylene which require some kind of isomerization step, than does catalyst 1. The effect of adding traces of cerium and potassium oxides to the two catalysts is not clear. The isomerizing power of catalyst 3 is drastically decreased while that of catalyst 1 is slightly increased. It has been reported that only minor amounts of cationic skeletal isomerization are obtained with a catalyst of low acidity, similar to catalyst 1.[3] Addition of these basic oxides to a catalyst will suppress cationic isomerization which requires acidic sites and which predominates over catalyst 3 whereas they perhaps enhance other isomerization mechanisms which appear to occur on catalyst 1.

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